Assessing and Tracking Nitrate Contamination from a Point Source and the Effects on the Groundwater Systems in Mid Canterbury, New Zealand

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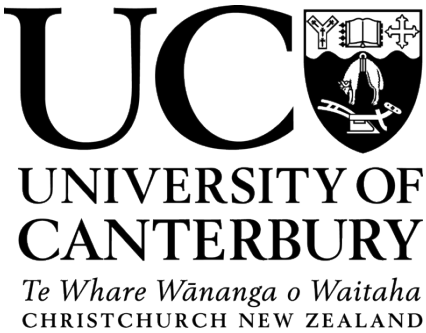

"Children of a culture born in a water-rich environment, we have never really learned how important water is to us. We understand it, but we do not respect it" – William Ashworth, 1982

Abstract

Water is a valuable and crucial resource, the protection of which poses environmental, social and economic challenges. Fundamental to the sustainable use of water is effective management. In the Canterbury region of New Zealand, nitrate contamination has become a resource management issue due to changes in land use and intensification, which have placed pressure on the region's groundwater and surface water systems.

The purpose of this study was to assess and track nitrate concentrations on the Central Canterbury Plains with specific emphasis on a local point source of nitrate, the Ashburton Meat Processors plant. To make this assessment review of historical data was followed by the collection of 131 groundwater and 25 surface water samples to analyse the geochemical properties of the water and the stable isotopic composition of nitrate in the water. It was hypothesised that nitrate concentrations at a regional scale have increased since regular records began and that the stable isotopic composition of different nitrate sources are not discernable.

Nitrate concentrations across the Canterbury region were found to have increased, prompting concerns about water quality. Concentrations are elevated above natural background levels across much of the Canterbury Plains and extreme concentrations are associated with local point sources of nitrate. Nitrate concentrations down gradient of the Ashburton Meat Processing plant are shown to have declined approximately 5% per year for the past ten years, which is in contrast to the rest of the region, where average concentrations have nearly doubled in 20 years. The reduction of contamination from the point source is most likely the result of the implementation of better wastewater management practices in the early 21st century.

The $\delta^{18}O$ and $\delta^{15}N$ values of nitrate were found to be relatively homogenous over the Canterbury Plains. Therefore, it is suggested by this study that the dual-isotope approach alone, is not a viable tool for nitrate source identification in the region. The uniform nitrate stable isotopic composition in Canterbury could be attributed to a single, principle source of nitrate, such as clover, that overprints other isotopic compositions of nitrate source, or may also be the result of soil processes and the farming techniques used in the region.

This research presents important findings for the future of identifying and managing nitrate sources in the Canterbury region. Better management practices are required for the diffuse source(s) of nitrate contributing to the widespread contamination. Critical thinking and the willingness of stakeholders to engage in the identifying, documenting and solving problems is necessary to ensure the effective management and sustainability of this precious resource.

Acknowledgements

There are many people whose support I must acknowledge, as without their time, assistance and understanding the thesis would never have been completed.

Firstly, thank you to my supervisor Dr Travis Horton, your support throughout is thoroughly appreciated. From providing new ideas and suggestions for research to helping out with fieldwork, analysing samples and assisting with shaping the final make up of the thesis. Also, in the department, thanks to Cristian Vasquez for helping out with field work and providing me with additional data when you moved on, to Christopher Oze and Josh Blackstock for providing ideas at various points, and to Janet and Pat for always being willing to help with the administrative tasks. Special thanks also to Megan Young at the USGS who completed the nitrate stable isotope analysis.

I must also thank my parents who have been with me every step of the way during my time at university, providing moral and financial support. They have always been available on the other end of a phone line to encourage me and keep me motivated. For this I am exceptionally grateful. Thank you also to all of the other family members both here in Christchurch and back home in Taranaki who have supported me along the way.

Also, to the many friends and colleagues who have been part of my university journey. In the department many people have made the experience enjoyable, with support, laughs or coffee breaks and discussion for the purpose of procrastination. To all of the flat mates I have lived with over the past couple of years that have made going home at the end of the day something to look forward to. Whether it was through helping me with university work, providing company, laughs and a great environment to live in, or putting food on the table after a tough day! Finally to the football refereeing community who often without realising it, were giving me a welcome relief from study either at a training session or during the pressures of match day.

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Chapter 1 - Introduction

1.1. Background

Water is a valuable and critical resource, especially in a region like Canterbury where the resource is abundant and readily accessible. Understanding the processes associated with the resource are vital for effective management. Poor management could lead to over-allocation of and deterioration in the quality of the water resource. This has already occurred to varying degrees in different localities, in Canterbury as well as globally, with a range of causes and consequences. One significant area of concern is the documented increase in nitrate concentration in the Canterbury region's water resources through time (Hanson 2002; Ford & Taylor 2006).

The Canterbury Plains is a flat, expansive, agriculturally productive region covering approximately 17000 square kilometres. It is a region that is an integral part of the manufacturing, agricultural, energy and tourism industries in New Zealand, particularly those in the agricultural sector. This is highlighted by the use of 97% of rural Canterbury land for agriculture, including 84% for pastoral land and 6% for dairying (Hill 2008). While agricultural productivity has increased markedly over recent decades, so have concerns regarding sustainability and consequences of this growth on human health. Of particular importance to the sustainability and health of Canterbury are possible alterations to the quantity and quality of water resources in the region. Rapid land use intensification is causing changes that are altering the landscape and environment in a manner that is difficult to compare with any other New Zealand setting.

Nitrate levels in many wells around the region have increased during the last 20 years and in some cases are reaching levels that exceed the maximum allowable value (MAV) of 11.3 mg/L nitrate-nitrogen (Ministry of Health 2008). The causes of the rise in nitrate levels

include both point sources and diffuse sources. Point sources occupy a very small area and have a concentrated output of waste. Located on the northern boundary of the town of Ashburton, three meat-processing plants are examples of point sources. These meat-processing plants were identified as the primary sources for nitrate plumes that are visible in down gradient groundwater. This water quality issue presents a unique opportunity to better understand how wastewater from a meat processing plant moves through an alluvial gravel aquifer.

1.2. Thesis Objectives

This thesis has four overall objectives:

1. To establish whether the use of stable isotope analysis of $\delta^{15}N$ and $\delta^{18}O$ allows the identification of nitrate sources to the groundwater in the Ashburton area.
2. To quantify the effects of various nitrate sources on the groundwater in Ashburton and put this into a wider context across the Canterbury Plains.
3. To combine stable isotope analysis with geochemical data in order to identify nitrate sources and track nitrate contamination.
4. To place water quality issues in Canterbury into a global context in terms of the challenges faced and the response to the issues.

1.3. Study Area

The town of Ashburton is located in Mid Canterbury, approximately 90 km south of the city of Christchurch. It is the major town in Mid Canterbury, New Zealand, and has a population of approximately 14500, with a further 12000 in the greater Ashburton District (Statistics New Zealand 2006). The town is a rural hub servicing the wider Mid Canterbury area. On the northeast boundary of the town there are three meat processing plants, reflecting the agricultural services focus of the town. All three companies possess permits which allow

them to discharge wastewater to the local groundwater system. This wastewater appears to have caused extreme increases in nitrate in the groundwater to above background levels. The increase in nitrate is macroscopically present as a plume of elevated nitrate water, down gradient from the discharge sites (Hanson 2002; Hayward & Hanson 2004). Nitrate contamination is an important issue for groundwater across the Canterbury Plains and the Ashburton Meat Processors (AMP) plume provides a case study from which a better understanding of point source discharge of nitrate into the groundwater system of the Canterbury region can be gained.

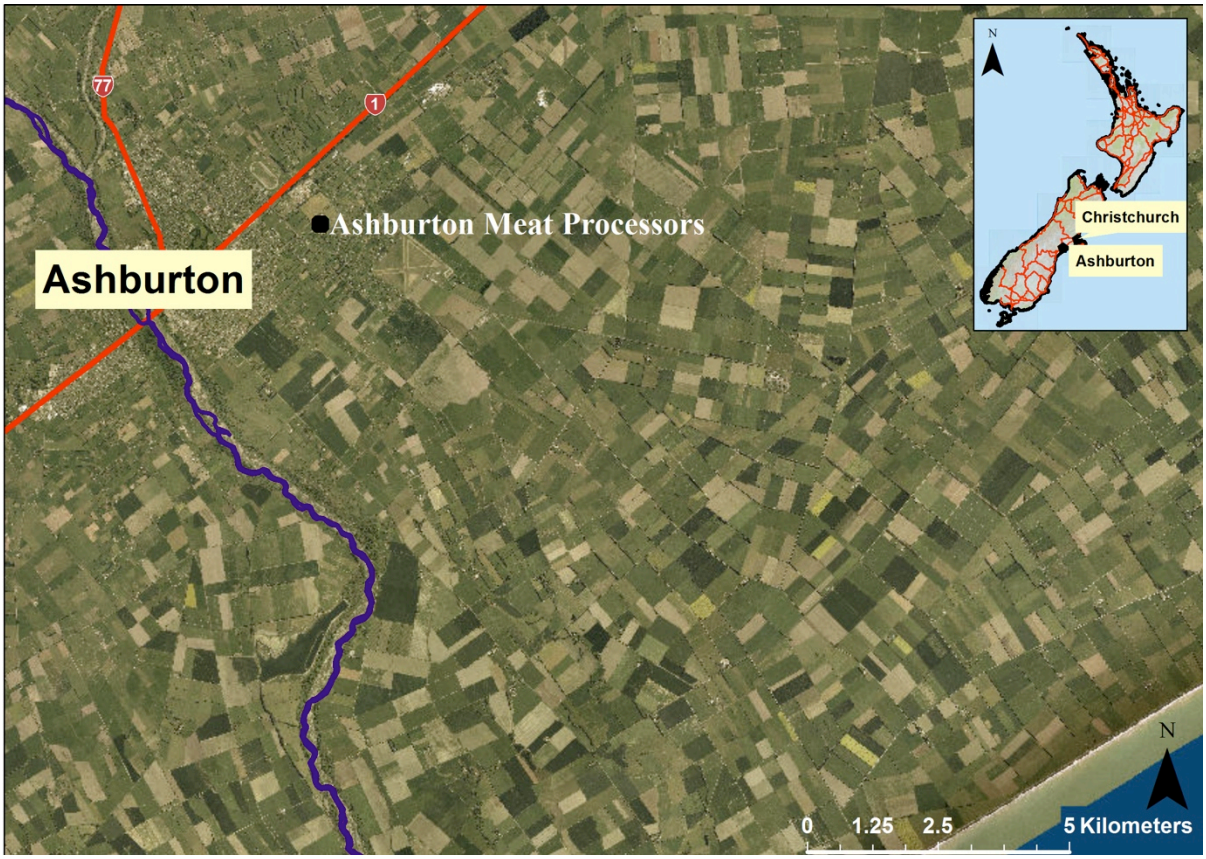

Figure 1.1 Map of New Zealand showing Central Canterbury Plains and the location of Ashburton on the Plains

Ashburton is located within the Canterbury Plains (Figure 1.1), an extensive gravel outwash plain. These plains support extensive farming opportunities and have been subject to increasingly intensive farming through a change from predominantly pastoral sheep to an increasing amount of dairy farming. Between 1995 and 2007, pastoral land had fallen from

73% to 53% of total rural land use, while in the same period dairying increased from 4% to 13% (Hill 2008). As a result, the groundwater system has been put under increased pressure in terms of both water availability and quality. On average, Canterbury dairy farms apply irrigation of 565 mm of water per year (Zonderland-Thomassen & Ledgard 2012) and have the highest stocking rates in New Zealand at 3.28 cows per hectare (Dynes et al. 2010). In order to regulate and control the use of groundwater, the wider system and processes controlling the system must be well understood.

1.4. Geology

The Canterbury Plains consist of deposits of up to 1,000 m thick Quaternary river and reworked glacial outwash. Between the Rakaia and Ashburton Rivers, an area covering approximately 1,350 km^2, Quaternary gravels cover Tertiary sediments and the basement greywacke (Brown & Weeber 2002)(Figure 1.2). The gravels are of variable permeability with layers of clay bound gravels between sandy gravels (Scott 1980). Correlation of these semi-confining layers between bore logs across the area is very difficult due to the high degree of spatial heterogeneity. However, persistent aquifer zones are present and produce water at 0-49m, 50-85 m and 130-160 m depth (Scott 1980; Stewart et al. 2002). There is a general trend of higher transmissivities both at shallower depths, and closer to the coast. These higher transmissivities are associated with younger gravels that can be linked to deposits from interglacial periods, where glacial outwash was reworked and transported further from their source rivers in the Southern Alps (Scott 1980; Fitzharris et al. 1992).

The geology across the wider Canterbury Plains is similar in its heterogeneity. Three significant braided rivers, the Rangitata, Rakaia and Waimakariri break up the plains. In the past the plains were created by the debris carried by these rivers from their headwaters at the main divide. Now the rivers flow over the plains, incising into the outwash gravels. The

Ashburton River is somewhat unique in that it once received, water draining from glaciers in both the Rakaia and Rangitata valleys created a wide local alluvial fan on the inlandp. As a result, the Ashburton River continues to flow over the top of its fan near the mountains, while other older and larger rivers have incised channels (Fitzharris et al. 1992).

Aquifer systems beneath the plains vary in their location, size and depth. Groundwater in the Canterbury Plains is largely unconfined, with some partially confined by relatively impermeable layers of finer sediments. Recharge to the aquifers occurs mostly from the alpine fed rivers described above, while rainwater contributions to groundwater recharge vary both spatially and temporally.

1.5. Climate

According to the Koppen system, Ashburton is subject to a warm temperate climate. The Southern Alps, which run northeast to southwest through the spine of the South Island, are the single most significant factor in determining the climate for the Canterbury Plains (NIWA 2012). High temperatures in Ashburton average 17.4°C annually, while low temperatures average 6°C. January is the warmest month, with an average high of 23.7°C, and July is the coldest month of the year, when average high and low temperatures are 10.7°C and 0.5°C respectively. Rainfall is relatively consistent across the year with an average of 57.99 mm each month. This is low when compared with the rest of New Zealand. Only September (43.7 mm) is significantly lower and April (65.5 mm) is notably higher than the mean (Casey 2007). The wind is predominantly of a westerly origin with the “nor’wester” weather pattern bringing strong winds in excess of 63 km/h, particularly in coastal areas. Winds are generally stronger inland, gusting to 160 km/h in extreme cases, especially along rivers where channelling occurs (Price 1993), while northeasterly winds prevail at the coast, and southwesterlies are common in winter months.

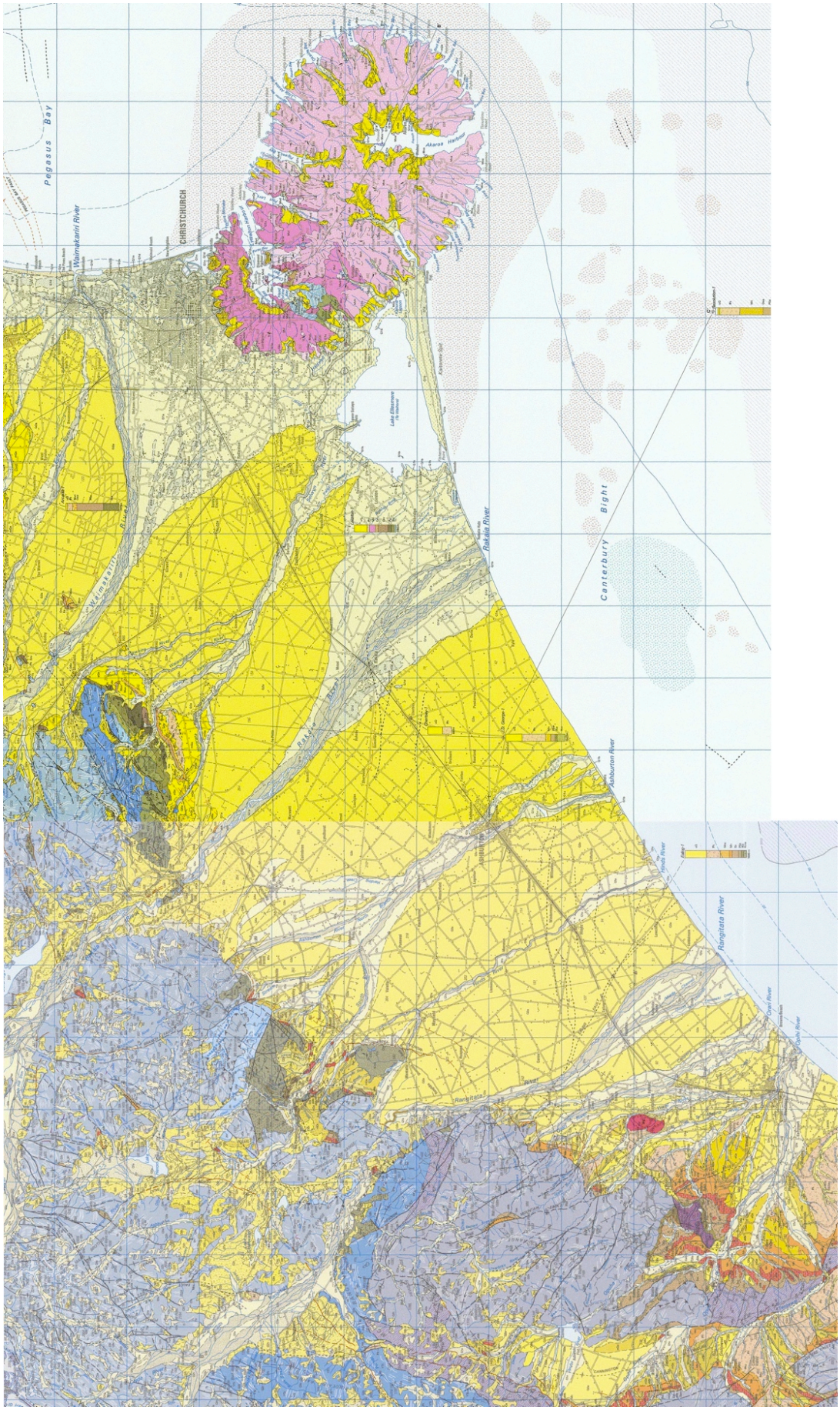

Figure 1.2 Geological Map of the Canterbury Region (Forsyth 2001; Forsyth et al. 2008) . For a full key see Forsyth 2001 and Forsyth et al. 2008.

1.6. Land Use

Land use in Canterbury has changed since early settlement in the mid 1800's. Over the past 30 years the change in the land use across the region has been dramatic. These changes are on going and are expected to continue over the next 20 years. Such rapid land use in turn has significant consequences for the environmental health of the land and the water and the way in which these are subsequently managed. For example, land that used for dairy farming increased from 20,000 ha in 1980 to close to 190,000 ha in 2009 (Figure 1.3). Production has also increased during this time, with a fifteen-fold increase in total production (Pangborn & Woodford 2011) and between 1994 to 2009 dairy cattle numbers increased six-fold (Dynes et al. 2010). Whereas through the 1970's and 1980's it was believed that most land in Canterbury was suitable only for sheep and cropping (Pangborn & Woodford 2011), modern land use is much more diverse. Higher production places more stress on the land and renders environmental management more challenging. Figure 1.3 highlights that the significant acceleration in conversion to dairy farming occurred in 1992, which has since seen a trend of about 10,000 ha, converted every year.

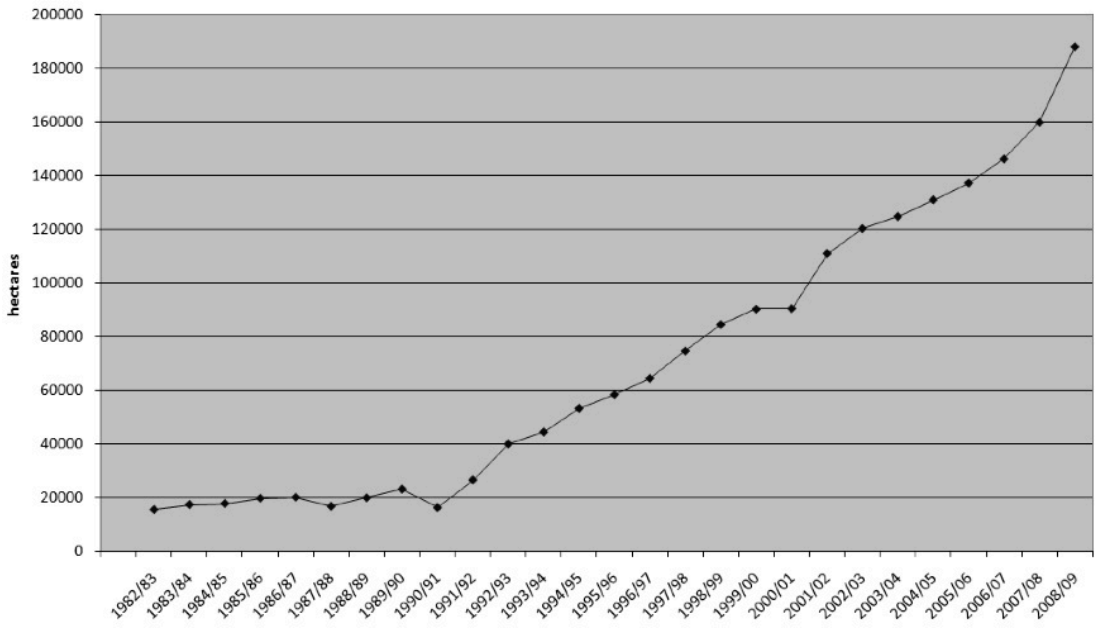

Figure 1.3 Area in ha of Dairy Farming in Canterbury 1982-83 to 2008-09, from Pangborn and Woodford 2011.

The lower land prices in Canterbury and advances in technology for irrigating land have driven change in land use. It has been estimated that about 400,000 ha of land in Canterbury is now irrigated (Pangborn & Woodford 2011). This comes from a mixture of community-based schemes accessing surface water, such as the Rangitata Diversion Race, that have been in use since the 1940's and both shallow and deep underground sources. Irrigated land is used for a variety of different farming types.

In the Ashburton District this trend of the wider Canterbury region is mirrored. Dairy farming has increased from 4% of the total rural land use in 1995 to 13% by 2007. Much of this has come from the reduction in pastoral land, which has undergone conversion to dairy. Pastoral is still the most significant rural land use, accounting for 53% of the land in the Ashburton District in 2007. Most of this land is however located in the high country as the other land uses are becoming dominant on the plains. The area of non-irrigated arable land has decreased by approximately 9,000 ha, offset almost perfectly by an increase in irrigated arable land (Hill 2008).

1.7. Research Questions

1. Are there spatial and temporal trends and patterns in the nitrate concentrations of the groundwater on the Canterbury Plains?
2. Are the $\delta^{15}N$ and $\delta^{18}O$ values of nitrate derived from a meat processing point source, statistically significantly different to diffuse area-sources of nitrate on the Canterbury Plains?
3. Are there elevated concentrations of nitrate down gradient from the Ashburton Meat Processing plant, and are these attributable to the deposition of waste material by the plant?

4. Are decreases in the groundwater nitrate concentrations down gradient of the Ashburton Meat Processors the result of dilution or microbial denitrification?
5. Are nitrate concentrations and sources in the Canterbury region comparable to similar settings worldwide, and are management practices implemented in an effective manner?

1.8. Thesis Methodology

The thesis work began with analysing data from the Environment Canterbury wells database. Surface and groundwater samples were collected from across the Central Canterbury Plains and analysed for nitrate-nitrogen concentration and other geochemical attributes. The $\delta^{18}O$ and $\delta^{15}N$ of nitrate in the samples was also determined in order to correlate the nitrate with a specific source. Groundwater and surface water from locations both up gradient and down gradient from the AMP plant were also collected and analysed. Spatial patterns in the nitrate concentrations and stable isotopes were then identified in the Ashburton area and across the Central Canterbury Plains through mapping and graphing of the data. These patterns were identified in order to establish the possible nitrate sources and its fate as it moved through the groundwater and interacted with surface water. The nitrate data was supported by other geochemical data including, chloride concentrations, and alkalinity. The data was also put into a global context by comparing it to data from other agriculturally intensive areas worldwide.

1.9. Thesis Format

This thesis is divided into five chapters. The second chapter reviews nitrate in groundwater, including sources of nitrate, effects on human health, and effects on the environment. Chapter two also includes a review of stable isotope and nitrate geochemistry and the techniques used in stable isotopic research. Chapter three presents an overview of the geochemistry of the

wider Canterbury Plains groundwater systems and also discusses the stable isotopic composition of groundwater in Canterbury, particularly in relation to nitrate. Chapter four is a more specific case study, addressing the AMP plume, its associated nitrate plume and how this has changed over time, using recently collected water samples and analysis of their nitrate concentration and stable isotopic composition. The final chapter presents my conclusions, including a summary of the research objectives and questions that were posed. In addition a brief discussion of the future is included.

Chapter 2 - Nitrates in Groundwater

Nitrate contamination of groundwater is becoming an increasingly significant issue both globally and here in New Zealand. Drinking water in Canterbury is largely sourced from groundwater, through distributed municipal supplies and domestic groundwater wells (Ashburton District Council 2010). The quality of this groundwater is therefore of great importance in terms of the sustainability of the resource, the health of the people who are drinking the water, and the health of the environment. Water quality will be and has been affected by the increased use of groundwater resources in the region, which in some zones are currently considered to be over allocated (Whitehouse et al. 2008). Land use intensification further stress the resource through increased fertiliser application and higher numbers of livestock present on farms (Hanson 2002; Hill 2008; Dynes et al. 2010; Pangborn & Woodford 2011). In order to understand the extent of nitrate contamination and the processes controlling nitrate distribution in groundwater and surface water systems, it is necessary to first understand the biogeochemical nitrogen cycle.

2.1. The Nitrogen Cycle

The nitrogen cycle (Figure 2.1) describes the movement of nitrogen through the earth system. Nitrogen can exist in several forms including as molecular gas in the atmosphere, the largest reservoir of nitrogen and smaller amounts of gaseous NO_2 and NO (Nieder & Benbi 2008). There are also several other reservoirs of nitrogen, including global oceans, surface water, groundwater, soils, and rock. These all have nitrogen locked in various forms and volumes. Numerous processes, both chemical and biochemical transfer nitrogen between these different reservoirs. These processes have been altered by human activities, which have changed the volume of nitrogen moving between and being stored in different reservoirs through time. For example, nitrogen entering the terrestrial ecosystem has doubled as a result

of industrial fixation of nitrogen, cultivating legumes that fix nitrogen and the burning of fossil fuels by humans (Nieder & Benbi 2008).

One important transfer of nitrogen is from the atmosphere to the biosphere. For assimilation into higher plants nitrogen requires combining with either hydrogen or oxygen (Canter 1997). This first requires nitrogen fixation, by breaking the N-N triple bond. Energy for this comes from both physical and biological processes (Nieder & Benbi 2008). Nitrogen movement in the soil is largely dictated by biologically, primarily microbiologically, controlled reactions including assimilation, nitrification and denitrification (Kendall 1998).

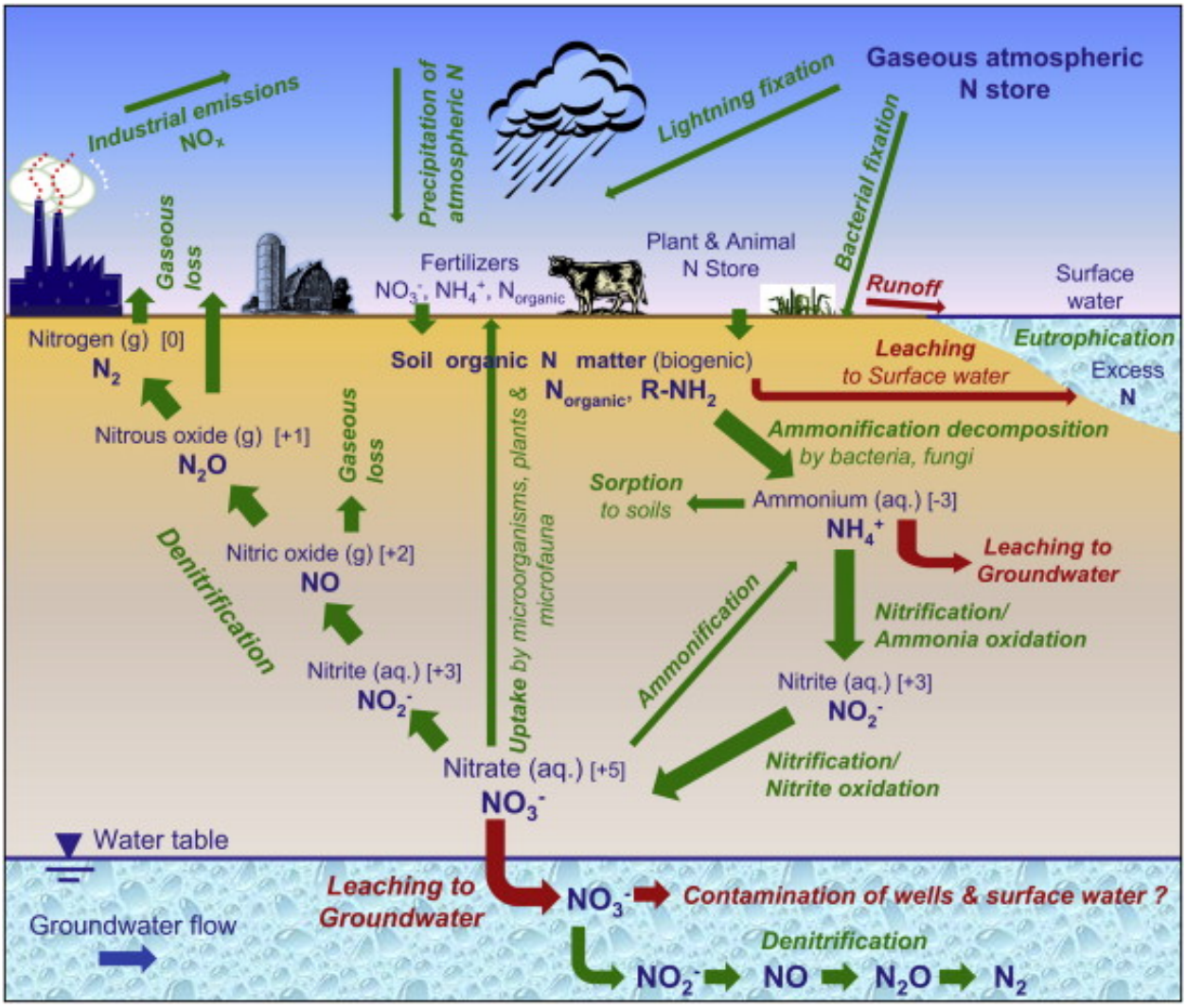

Figure 2.1 The Nitrogen Cycle (Rivett et al. 2008).

2.1.1. Nitrogen Fixation

The fixation of nitrogen, converting N_2 to NH_3, is a process that sees atmospheric nitrogen incorporated into a chemical compound making it available for use by plants and animals. This process takes place in three main ways, lightning, biological and industrial.

Biological processes are the dominant natural mechanisms for fixation, though industrial and lightning fixation are also significant in their contribution. Fixation through biological processes is carried out by nitrogen fixing bacteria, either in a symbiotic relationship with plants such as legumes or free-living bacteria in the soil. The bacteria involved are known as diazotrophs and conversion to ammonia (NH_3) is carried out by the enzyme nitrogenase (Kim & Rees 1992). Significantly more nitrogen is fixed by the bacteria living in symbiosis with plants than those that are free-living, due to the energy required for the reaction. Through living in symbiosis the bacteria are able to draw the energy from the plants. In New Zealand, legumes and clover have been used effectively in agriculture in order to increase productivity through higher nitrogen production (Ledgard et al. 2009; de Klein et al. 2010).

Lightning fixation causes N_2 and O_2 to combine and form NO through high pressure and temperature. Following fixation the NO is oxidised to form NO_2 and eventually HNO_3. Deposition into ecosystems from the atmosphere then occurs quickly, within days after this transformation (Galloway et al. 2004), though only a portion is deposited terrestrially, most is deposited into the oceans (Schlesinger 1991). Fixation by lightning is most important in locations where there is a lack of other nitrogen sources to an ecosystem.

Anthropogenic industrial fixation of nitrogen by the Haber-Bosch process is the final way in which nitrogen is fixed and now exceeds natural biological nitrogen fixation. Human use of nitrogen is in the production of food, plastics, refrigerants, synthetic fibres, explosives, with a significant majority being in the production of nitrogen fertilisers. Nitrogen fertilisers account

for 86% of the total nitrogen fixed by the Haber-Bosch process (Nieder & Benbi 2008). The industrial nitrogen fixation process is similar to the natural process where nitrogen is fixed by lightning, using high temperature and pressure. As a result of the process NH_3 is produced and then combined with other compounds to form different types of nitrogen fertilisers.

Once fixed, nitrogen can be taken up by plants and then ingested by plant eating animals. As nitrogen is an essential element required by all known forms of life, the nitrogen fixation process is fundamental to the life supporting capacity of natural systems.

2.1.2. Nitrification

Nitrogen that has been converted to ammonia through fixation may then be nitrified through a series of steps. First ammonia is converted to ammonium by ammonification, second ammonium is converted to nitrite and finally nitrite is converted to nitrate by biological oxidation (Canter 1997; Rivett et al. 2008). Each of these steps involves microbiological organisms and can be summarised by the following equations:

$$NH_3 \rightarrow NH_4^+ + O_2 \xrightarrow[bacteria]{Nitrosomonas} NO_2^- + O_2 \xrightarrow[bacteria]{Nitrobacter} NO_3^-$$

The completion of the above reactions requires oxygen, which is restricted by the amount of moisture filling pores in the soil, therefore soil moisture dictates the ability for the reaction to take place and the reaction speed. Formation of both nitrite and nitrate produces energy that the bacteria nitrosomonas and nitrobacter use for their life functions. The various interim steps of nitrogen compounds may be taken up by plants or undergo sorption to the soil. Any remnant NH_4^+, NO_2^- and NO_3^- can then be leached into the ground or surface water.

2.1.3. Denitrification

The nitrogen cycle is completed by denitrification, the biologically facilitated chemical reduction process converting nitrate or nitrite to nitrogen gas (Van Spanning et al. 2005). Denitrification is a combination of several steps that transform nitrate to nitrite, nitrite to

nitric oxide, nitric oxide to nitrous oxide, effectively acting as the reverse of nitrification (Canter 1997; Van Spanning et al. 2005). Again, bacteria carry out most nitrate reduction, with a very minor amount occurring through abiotic reactions. Organisms that are capable of denitrification are common in surface water, soils, and groundwater to a considerable depth. Other than nitrite, all of the interim products are gases. These gases can be discharged to the atmosphere. These products are important, as the denitrification may be arrested at any of the intermediate steps and not proceed through to its stable end product of nitrogen gas. Nitrous oxide gases are environmentally harmful and nitrite is more toxic to humans than nitrate (Rivett et al. 2008). Biogeochemical conditions of the subsurface at any given location will affect the extent of denitrification, including its speed and which nitrogen compound will form the end product. An ideal conceptual model of denitrification in the subsurface is shown in figure 2.2 (Rivett et al. 2008) and highlights the conditions where denitrification is most likely. Subsurface denitrification varies over space and time and can lead to the reduction in nitrate and nitrite concentrates in the soil or groundwater.

Denitrification processes are restricted and controlled by a number of different environmental factors, with the two most significant influences being the availability of oxygen and of nitrogen oxides. Other factors less significant but still influential factors include, pH, soil water content, temperature, porosity and the existence of inhibitory compounds (Van Spanning et al. 2005). This multitude of factors means that predicting the occurrence and extent of denitrification is challenging.

Importantly, the concentration of nitrate will also affect the denitrification process. Nitrate must be present for denitrification to occur, though if there is an excessive amount of nitrate present, denitrification can be inhibited at the final stage, meaning that nitrogen gas is not produced and the final product is nitrous oxide. This negative feedback on denitrification is site specific and depends on many other factors as well (Rivett et al. 2008).

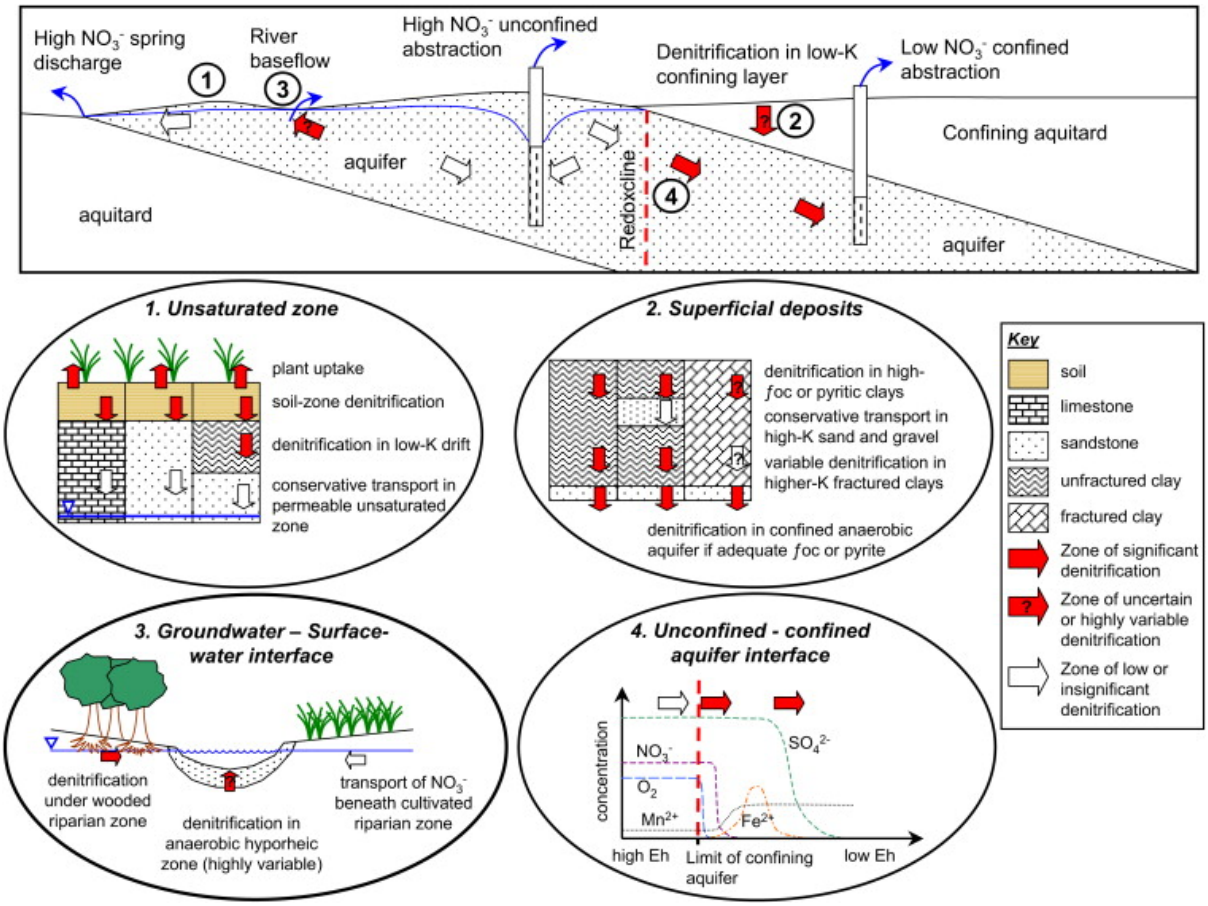

Figure 2.2 Denitrification in the subsurface - A conceptual model (Rivett et al. 2008)

In addition to high levels of nitrate, dissolved oxygen concentrations above 4 mg/L-O_2 may limit the denitrification process at the various stages. This is due to denitrification being a less favourable reaction than the chemical reduction of dissolved oxygen. A primary control on the availability of oxygen is the water content of soil (Van Spanning et al. 2005). When soil is saturated in water, there is less pore space for oxygen to move through the soil. As a result beneath the water film, there will be pockets where there is less free oxygen. The conditions in turn promote the growth of denitrifying bacteria.

Low pH values can also limit the denitrification process (Van Spanning et al. 2005). Denitrifying bacteria have a preferred pH range between 5.5 and 8.0 (Rust et al. 2000). If pH is not within this range then denitrification can be hindered, however this is once again site specific and denitrifying bacteria can adapt to function outside of the preferred range

suggested by Rust et al. (2000). If the environment is strongly acidic then the denitrification process may be stopped altogether at the nitrite or N_2O stage of the denitrification process (Rivett et al. 2008).

Temperature may also affect the rate of denitrification in the subsurface. The ideal temperature for denitrification to occur is between 25 and 35°C, though the process will likely still occur between temperatures varying between 2 and 50°C. This range may however be extended even further when bacteria are able to adapt to the environment that they are in (Rivett et al. 2008). Groundwater temperatures are relatively stable and therefore this tends not to alter denitrification rates. In Canterbury, groundwater temperatures are around 12 °C (Stewart et al. 2002) similar to the mean annual air temperature.

In addition to the physic-chemical controls on denitrification, inhibitory substances or compounds that are toxic to the denitrifying bacteria, as well as substances like heavy metals and pesticides (Van Spanning et al. 2005; Rivett et al. 2008) may limit the extent of denitrification. Elevated levels of some substances such as cadmium, copper, lead and zinc, common elemental compounds in most fertilisers (McBride & Spiers 2001) inhibit denitrification to varying levels. Pesticides meanwhile have variably affected the extent of denitrification in various systems (Rivett et al. 2008).

2.1.4. Nitrogen Leaching to Groundwater

Nitrogen that is not taken up by plants, incorporated into the soil or lost to the atmosphere can be leached to the groundwater (Di & Cameron 2002). This nitrogen loading is occurring in many places around the world (Nieder & Benbi 2008). Nitrate is the most frequent form of nitrogen to be leached as a result of ammonium being readily converted to nitrate in well oxygenated near-surface systems (Di & Cameron 2002). Importantly, nitrate can also be leached to surface water and interactions between surface water and groundwater, as occur

throughout the Canterbury Plains, can make identifying and tracking sources more complex. The manner and amount of nitrate that is leached to groundwater is dependent on the source flux of nitrate as well as the environmental conditions such as soil type, vegetation type, rainfall and irrigation. The nitrogen cycle is a complex combination of processes and transformations that have a number of limiting factors that make studying parts of the cycle in natural systems inherently challenging.

2.2. Nitrate Sources to Fresh Water

Given the complexity of the wider nitrogen cycle, it is instructive to focus on the nitrate molecule. There are a number of different sources of nitrate to groundwater including, natural soil nitrate, waste material, row crop agriculture and irrigated agriculture. In Canterbury, it is likely that each of these contribute to the regions water quality issues to varying extents. Identification of nitrate sources is an important first step for both the remediation of any contamination and to put in place controls to reduce effects in the future. The area of groundwater contaminated and the level of contamination varies with each different nitrate source. Most nitrates from waste material originate from a point source and therefore the effects tend to be spatially discrete. Diffuse sources are typically derived from a much wider area and, although the concentrations of nitrate may not be as high, identifying the source and implementing any clean up or remediation measures can be significantly more challenging.

2.2.1. Natural Nitrate

Nitrate originating from nitrogen fixing plants and microbes, and from rocks can be classified as natural nitrate. The overall effect of the natural nitrate has on the local environment will depend on the geological and biological setting.

While the nitrate occurring as a result of fixation and nitrification is a natural process, humans have altered its significance by controlling when and where certain plants are grown.

Plants such as clover are planted with grass on land where it is desirable to raise the nitrogen content of the soil (Tillman 1998). When the plant dies, this nitrogen is released into the soil during decomposition and is ultimately available for other plants to utilise. A system in equilibrium will rely on this internally recycled source of nitrogen and neither gain nor lose excess nitrogen fixation and nitrification or leaching respectively

In some locations nitrate in the water may be sourced from rocks that come into contact with the water. While a majority of global nitrogen is in the atmosphere, there is also a significant portion, approximately 20% is locked in sedimentary rocks which account for 75% of the rocks exposed to the Earth's surface (Holloway et al. 1998). This seems unlikely as a nitrate source to water in Canterbury as there are no records of the common nitrogen mineral compounds being present in the sedimentary rocks of the region (Wandres et al. 2005).

2.2.2. Anthropogenic Sources

There are several anthropogenic sources of nitrate. This can include nitrate from a natural source that is increased by human activities. Human modification of the nitrogen cycle has been steadily accelerating since 1920, affecting different components of the cycle to varying degrees, the consequences of which are only now beginning to be entirely understood. Anthropogenic nitrate can be separated into, fertilisers, animal manure, septic waste and nitrate from industrial activities and food production.

Nitrogenous fertiliser is an anthropogenic nitrate source that has a variable effect on the land and water depending on management practises. For example, different types of fertiliser with different nitrogen contents are used depending on what modifications are required for the particular soil type and the desired land use productivity. In New Zealand several different types of fertiliser are used, including lime, phosphate, superphosphate and nitrogenous fertilisers (Statistics New Zealand 2006). The use of nitrogenous fertiliser in New Zealand

has increased by a factor of ten since 1985 as a result of land use becoming more intensive (Ministry for the Environment 2007). Given the relatively slow movement of water through groundwater systems, it is possible that we are just now beginning to observe the consequences of these actions.

Manure and animal waste are viewed as anthropogenic sources of nitrate due to the nature of intensive farming and agriculture that leads to there being nitrate above the natural background levels. Urine deposits from stock are often not evenly distributed leaving patches that are highly concentrated in nitrogen. The nitrogen is in the form of ammonia and after being deposited by stock it is possible for this ammonia to undergo volatilisation. This converts the ammonia to ammonium and the ammonium to nitrate (Lockyer & Whitehead 1990). The nitrate can then either runoff into surface water or leach into the soil and groundwater. The nitrogen content of the urine will generally reflect the diet of the animal and in most cases the nitrogen being returned to the soil is in excess of the pastures requirement. Diets of animals such as dairy cows are likely to have high nitrogen content due to the desired increase in milk production. This leads to more nitrogen that will be lost either to the atmosphere or water, and not absorbed by plants (de Klein et al. 2010).

2.3. Effects of Nitrate Contamination on Human Health

Nitrate contamination of groundwater is of concern due to the detrimental effects to human health. Water is a precious and necessary resource and protecting its health for the human health is important, whether it be by identifying and managing contamination sources or treating contaminated water. As a result of the health risk the World Health Organisation have recommended a maximum value for nitrate in drinking water of 11.3 mg/L of nitrate-nitrogen (50 mg/L nitrate). This standard is subsequently used by the Ministry of Health in New Zealand as the drinking water Maximum Allowable Value (MAV) (Ministry of Health

2008). Values that are in the range of 40 – 100 mg/L of nitrate-nitrogen are considered to be of high risk (Di & Cameron 2002). Health risks for humans include methemoglobinemia (particularly in infants) and cancer.

Methemoglobinemia or 'blue-baby syndrome' occurs if levels of methemoglobin reach a point in the blood where the oxygen carrying capacity of the blood will be affected. When nitrate is consumed, it is converted to nitrite and combines with haemoglobin to form methemoglobin (Ward et al. 2005). Methemoglobin does not carry oxygen and therefore leads to the oxygen deficiency (Loo & Wen 2005). This is more susceptible to occurrence in infants due to their increased ability to convert nitrite to nitrate and a lesser ability to convert methemoglobin to haemoglobin (Ward et al. 2005). The reduced oxygen in the blood will cause the skin to turn blue, giving rise to the term 'blue-baby syndrome'.

There have been several attempts to establish whether there is any correlation between exposure to elevated nitrate in drinking water and various forms of cancer. The results of these studies are vaariable, including positive relationships, no relationship and even inverse relationships. Other factors and influences may either enhance or oppose the chance of nitrate increasing cancer risk, though this is not well understood (Ward et al. 2005). It is therefore believed that while consuming excessive levels of nitrate may be a contributing factor to cancer, other factors are more influential and may need to occur concurrently, for the risk to be increased.

Similarly, the understanding of the effects of nitrate in drinking water on reproductive outcomes is not well understood. Studies into neonatal births, stillbirths, and congenital anomalies have been undertaken and shed little light onto whether nitrates pose any risk and whether there are other contributing factors (Ward et al. 2005). Further research is being

undertaken to establish whether there is a relationship between excess nitrate consumption and complications during pregnancy.

2.4. Nitrate Effects on the Environment

Excess nitrate in water can have detrimental effects on the environment, including cultural eutrophication (Di & Cameron 2002). Eutrophication occurs in surface water when added nitrogen or phosphorous causes an increase in production of plants in water bodies such as rivers, lakes or coastal areas (Statistics New Zealand 2006). The process is natural in some surface water bodies, however cultural activities can increase the rate of eutrophication and the process can be much more dramatic (Perry & Vanderklein 2009). Nitrogen and phosphorous are limiting nutrients and increases in these lead to greater plant and algal primary production. If this occurs to a significant level harmful algal blooms may occur (Perry & Vanderklein 2009). Large algal blooms can cause deterioration in habitat quality, a reduction in available oxygen and an increase in toxins in some species such as shellfish, depending on the algae involved. As a consequence some animal life in the water may not be able to survive, due to reduced dissolved oxygen concentrations. There may also be effects on recreational use in water bodies, as well as their ability to provide drinking water. In many locations, including Canterbury eutrophication occurs in coastal waters as the nutrients are carried across the plains by rivers and then discharged in the coastal environment (Ford & Taylor 2006). Additional algal blooms occur are known to occur in New Zealand waters, although their cause is not fully understood and more work is required in order to establish any relationship between algal blooms and nutrient loading in the Canterbury region.

2.5. Effects of Geology on Groundwater Quality Vulnerability

Contamination of surface water is much more common than in groundwater due to the lower vulnerability of aquifers to pollution. However, when pollution does occur in groundwater it

is much more difficult to remediate and the contamination is often long lasting. This is a consequence of the inaccessibility of groundwater as well as the larger storage volume and extended storage periods (Foster & Chilton 2003).

At high spatial resolution, the vulnerability of a particular aquifer is difficult to establish and can be broken into two main factors. These are the natural factors influencing the aquifers susceptibility, and the relationship that the pollutant has with the environment and geology (Poicene & Pocius 2005). The filtration characteristics of the upper soil, the depth of the aquifer and ground relief will all affect the ability of the soil to reduce the pollutants effects on the groundwater. It has been recognised that the subsurface has the potential to act as a safe system for the disposal of waste and wastewater. The complexity that arises is that not all soils are equally effective at mitigating pollution (Foster & Chilton 2003; Poicene & Pocius 2005). As a result, there is always some risk with depositing wastewater onto land, without prior knowledge of the soil's ability to mitigate against the pollutants. If the soil is unable to filter out any harmful substances then these can end up in the groundwater.

In Canterbury there has been some assessment of the vulnerability of the various aquifer (Ford & Taylor 2006). Aquifers most at risk are the shallow unconfined aquifers as they are more readily influenced by the land use above them, due to the shallow water table, thin soils with little organic matter, and highly permeable overlying gravels and sands. The deeper parts of the unconfined aquifers or the semi-confined aquifers are a moderate risk of contamination. Risk for these aquifers comes from contaminants that are more persistent or mobile. There is some internal protection if the aquifer is semi-confined through an upward pressure gradient and a lower permeability of the overlying layer. Coastal confined aquifers are much lower risk as they have a stronger upwards pressure gradient and fine overlying layers with low permeability. Their vulnerability can be increased if they pressure is reduced

through over-abstraction, or if recharge areas are open to contamination (Ford & Taylor 2006).

2.6. Stable Isotopes and Nitrate

In order to manage water quality, it is important to be able to identify sources of pollution and subsequently trace the effects of the pollution. Stable isotopes are able to provide significant information about the Earth, its systems and processes, and the environmental health of those systems. They can act as tracers and proxies, and can therefore be used to interpret past systems and better understand current processes. It is becoming possible through the use of stable isotopes to quantify residence times of various constituents in the ocean, atmosphere and other reservoirs. As understanding has grown stable isotopes have become a powerful tool in environmental geochemistry particularly when complemented by other tracers (Porcelli & Baskaran 2011).

2.6.1. Properties of Stable Isotopes

It is possible for atoms of the same element to have different numbers of neutrons and subsequently a different atomic mass. These variants of the same element are known as isotopes (Kendall & Caldwell 1998). In most cases the stable isotopes of different elements will consist of one isotope that is overwhelmingly abundant along with one or two other isotopes that are much less abundant (Dawson & Brooks 2001). For example the abundant isotope of hydrogen is ^{1}H, which has a mass abundance of 99.985%, while the heavier isotope, ^{2}H only has an abundance of about 0.015%. Similarly, the light isotope of oxygen, ^{16}O, has a mass abundance of 99.762% and the heavier isotopes, ^{17}O and ^{18}O, have mass abundances of 0.0379% and 0.200%, respectively (Gat 2010). Stable isotopes differ from radioactive isotopes, as they are energetically stable and thus do not decay to daughter isotopes. Nuclear stability usually occurs because the number of neutrons and protons in an atom are similar (Sulzman 2007). Enrichment in the lower abundance isotopes can provide

the opportunity to use the element as a tracer in environmental science. The lighter elements are commonly applied in environmental research as they are common in materials and naturally occur in liquids, solids and gases. Stable isotopes also have the ability to provide information over differing temporal and spatial scales adding to their versatility (Leibundgut et al. 2009).

2.6.2. Isotopic Fractionation

When any dynamic process occurs there is the possibility that the abundance of a particular isotope in the molecules involved in the process will change. The change in abundance of one isotope relative to another as a result of such a process is called isotopic fractionation. Isotopic fractionation occurs in both systems at equilibrium and in processes driven by kinetic effects (Gat 2010). Thus, mass dependent fractionation can be broadly separated into isotopic equilibrium exchange, and kinetic fractionation (Dawson & Brooks 2001; Gat 2010).

2.6.3. Equilibrium Fractionation

Equilibrium reactions lead to a difference in the isotopic composition of two compounds with respect to a common element, when the reaction that causes the isotopic exchange is in chemical equilibrium. The ratios in each compound of the various isotopes are constant for a particular temperature. This is demonstrated by the equation:

$$AX^0 + BX^1 \quad \leftrightarrow \quad AX^1 + BX^0$$

Where X^0 and X^1 indicate the two different heavy and light isotopes of the common element. This occurs in closed, well-mixed systems where the reaction is reversible and the isotopic ratios vary between phases of the same substance. In the different phases of a substance it is usual for the more dense material, or that with the stronger bonds, to be enriched in the heavier isotope, for example $\delta^{18}O$ will be more positive in ice than in liquid water, which will

in turn be more positive than water vapour (Kendall & Caldwell 1998; Dawson & Brooks 2001; Gat 2010).

2.6.4. Kinetic Processes

Kinetic isotopic fractionation is an irreversible, unidirectional process that depends on the masses and the associated total kinetic energies of the isotopes. These kinetic effects are often much larger than equilibrium fractionations and tend to cause a relative accumulation of the lighter isotope in the reaction product(s), while residual reactants tend to be enriched in the heavier isotope, relative to the original unfractionated composition. This is due to the lighter isotope being able to vibrate and dissociate more readily. Several processes can be described as kinetic fractionations including evaporation, diffusion, dissociation reactions and enzymatic effects (Kendall & Caldwell 1998; Sulzman 2007). Kinetic fractionations are the dominant isotopic effects associated with the nitrogen cycle.

2.6.5. Nitrogen Stable Isotopes of Nitrate

Nitrogen on Earth is distributed such that 97.76% of all of the Earth's nitrogen is in rocks, 2.01% in the atmosphere and the rest in the hydrosphere and biosphere (Kendall 1998). There are two stable isotopes of nitrate, ^{14}N and ^{15}N. There is a significant range of valence states for nitrogen, between +5 and -3. This then results in several different compounds that include nitrogen and subsequently a wide range of isotopic compositions. The natural occurrence of each of the two stable isotopes of nitrogen is approximately 99.6337% for ^{14}N and 0.3663% for ^{15}N (Kendall & Caldwell 1998). Nitrogen isotopic values are shown using delta notation from the following equation:

$$\delta^{15}N\ [‰] = [(^{15}N/^{14}N_{sample})/(^{15}N/^{14}N_{reference}) - 1].1000$$

The reference for nitrogen isotopes is AIR, in other words atmospheric nitrogen. Delta values are normalised to this absolute reference composition (Sigman et al. 2001). Numerous

techniques have been developed for the gaseous extraction of the nitrogen and oxygen in aqueous nitrate to allow isotopic ratio determination using an isotope ratio mass spectrometer (IRMS).

2.6.6. Oxygen Stable Isotopes of Nitrate

There are three different stable isotopes of oxygen, ^{16}O, ^{17}O and ^{18}O. The isotopic ratio of oxygen is shown using the following equation and the delta notation:

$$\delta^{18}O\ [‰] = [(^{18}O/^{16}O_{sample})/(^{18}O/^{16O}_{reference}) - 1].1000$$

$\delta^{18}O$ values are reported relative to Vienna Standard Mean Ocean Water (VSMOW).

Microbially produced NO_3 usually has $\delta^{18}O$ values determined by the $\delta^{18}O$ of atmospheric oxygen and water. Theoretically NO_3 microbially formed will receive one oxygen atom from the atmosphere and two from H_2O (Xue et al. 2009). Atmospheric oxygen has an $\delta^{18}O$ value of about +23‰. There is however a significant range in values of $\delta^{18}O$, owing to oxygen originating from other sources, such as soils and streams, as well as fractionation occurring during various processes. The oxygen isotopes are most useful for distinguishing between atmospherically derived nitrate and microbially derived nitrate as the values are so far separated with no overlap (Xue et al. 2009). It is also possible to separate the synthetic nitrate sources from other sources.

Different oxygen isotope compositions in nitrate are the result of different processes that affect it in the nitrogen cycle. In theory nitrate that is the result of nitrification should show $\delta^{18}O$ values of -10 to +10‰ due to the contribution of both water and atmospheric oxygen to the oxygen in NO_3 (Xue et al. 2009). This is not always the case though, with the $\delta^{18}O$ of nitrate produced by microbes known to be as much as 5‰ higher than the theoretical maximum. This is likely to be the result of the oxygen in the water being enriched through

evaporation prior to nitrification. More positive $\delta^{18}O$ values of oxygen in the soil water are often the result of plant respiration that causes fractionation. Significant fractionation as the water and oxygen combine to form nitrate may also lead to more positive values of $\delta^{18}O$ (Xue et al. 2009).

2.7. Analytical Techniques for Nitrate Stable Isotopes

As mentioned above number of different techniques have been used in order to determine the stable isotopic composition of nitrate in water samples. This remains a developing science and newer methods continue to improve accuracy while reducing the cost, time and preparation involved for the analysis. These techniques include the bacterial denitrification method, the ion exchange method and the cadmium reduction method. Each of the methods converts nitrate into a gaseous phase, a fundamental requirement of all modern isotopic analytical equipment.

2.7.1. Bacterial Denitrification Method

The bacterial denitrifier method produces $N_2O_{(g)}$ from the $NO_{3(aq)}$ using denitrifying bacteria. Oxygen and nitrogen isotopic compositions can then be determined from the resulting N_2O. Conversion of the nitrate to N_2O involving the following steps:

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O$$

The process begins with the preparation of the microbiological denitrifier cultures. Two different bacteria can be used in the denitrification process, *Psuedomonas chlororaphis* and *Psuedomonas aureofaciens*. Each species has its advantages, *P. chlororaphis* is more robust in culture, but die not allow for the oxygen isotopes of nitrate to be determined in addition to the nitrogen isotopes, while *P. aureofaciens* does allow for this (Sigman et al. 2001). An excellent summary outline of the process involved in the preparation and implementation of the process is given by Sigman et al. (2001) and Casciotti et al. (2002).

During bacterial denitrification isotopic fractionation occurs for both the nitrogen and oxygen isotopes. These fractionations are an unavoidable consequence both in the laboratory and the natural systems. In the case of the nitrogen isotopes, this is not a concern if the conversion of NO_3 to N_2O is complete and there are no other pools of nitrogen that could be undergoing conversion to N_2O. In other words, the mass concentration between the reactant and the product means that the fractionation will not be expressed in the isotopic results (Sigman et al. 2001). However, in the case of oxygen there is only one of the original six oxygen atoms from the initial nitrate present in the N_2O product. Therefore if ^{16}O is lost preferentially in the reaction sequence then there will be a difference in the isotopic composition of the NO_3 and the produced N_2O. To correct for this, the fractionation must be reproducible over a given batch of analyses. A second concern is that exchange of oxygen atoms can occur between the N_2O intermediates and water. This would then introduce oxygen atoms that do not represent the original nitrate. Therefore corrections must be made for the exchange of the oxygen atoms with water (Casciotti et al. 2002).

The product N_2O is analysed for $\delta^{15}N$ and $\delta^{18}O$ either by cryo-concentrating and extracting the N_2O through freezing it out in a vacuum line and analysing using isotope ratio mass spectrometry (Xue et al. 2009). The data reported in this thesis was determined using the USGS stable isotope lab (Menlo Park, California, USA) under the direction of Carol Kendall.

2.7.2. Ion Exchange Method

The ion exchange method also involves the conversion of NO_3^- to N_2, for analysis. It is also commonly know as the "Silver Exchange Method" and was proposed in 1999 and 2000 (Chang et al. 1999; Silva et al. 2000). The method involves the concentration and purification of the nitrate in the water samples. This allows the analysis of both the $\delta^{15}N$ and $\delta^{18}O$ isotopes of the nitrate.

Samples are passed through both anion and cation exchange resin columns. The nitrate is then remobilised through the use of hydrochloric acid and AgO is used to neutralise eluent. Silver chloride is then removed by filtering. Any non-nitrate anions that contain oxygen must then be removed either oven or freeze-drying then produces salts of $AgNO_3$. To analyse for $\delta^{15}N$, NO_3^- is converted to N_2 gas by mixing with CuO and then combusting in a sealed tube at 850°C. While analysis of $\delta^{18}O$ is completed using the combustion method and adding finely ground graphite to produce CO_2 (Chang et al. 1999).

There are several disadvantages with this method, leading to its diminishing use in more recent times. Preparation is both cost and labour intensive, and there is the chance of interference with the sorption of NO_3^- onto exchange resins due to the high anion concentrations. Perhaps most limiting is that if the concentration of nitrate in the samples is low then a very high volume of water sample (Xue et al. 2009), sometimes more than 7 litres that is required (Chang et al. 1999).

2.7.3. Cadmium Exchange Method

The cadmium exchange method, also known as the azide method involves the change from nitrate to nitrite and then to from nitrite to nitrous oxide for analysis. Initially, reaction with spongy cadmium causes the reduction from nitrate to nitrite. Following this, the nitrite is reacted with sodium azide to produce nitrous oxide. The produced N_2O is analysed in the same manner as for the denitrifier method (McIlvin & Altabet 2005; Xue et al. 2009).

The advantages of this method are in its ease of use. There is little lab preparation time required, it is possible to automate if there is a high sample throughput, and only low concentrations and volumes are required for analysis. However, there are several negative aspects, including, issues both environmentally and to health associated with the toxicity of the substances used in the reactions, the requirement of corrections for the exchange and

fractionation of oxygen, and the presence of any nitrite in the water could alter the isotopic composition of the end nitrous oxide (Xue et al. 2009).

2.8. Stable Isotopes for Nitrate Source Identification

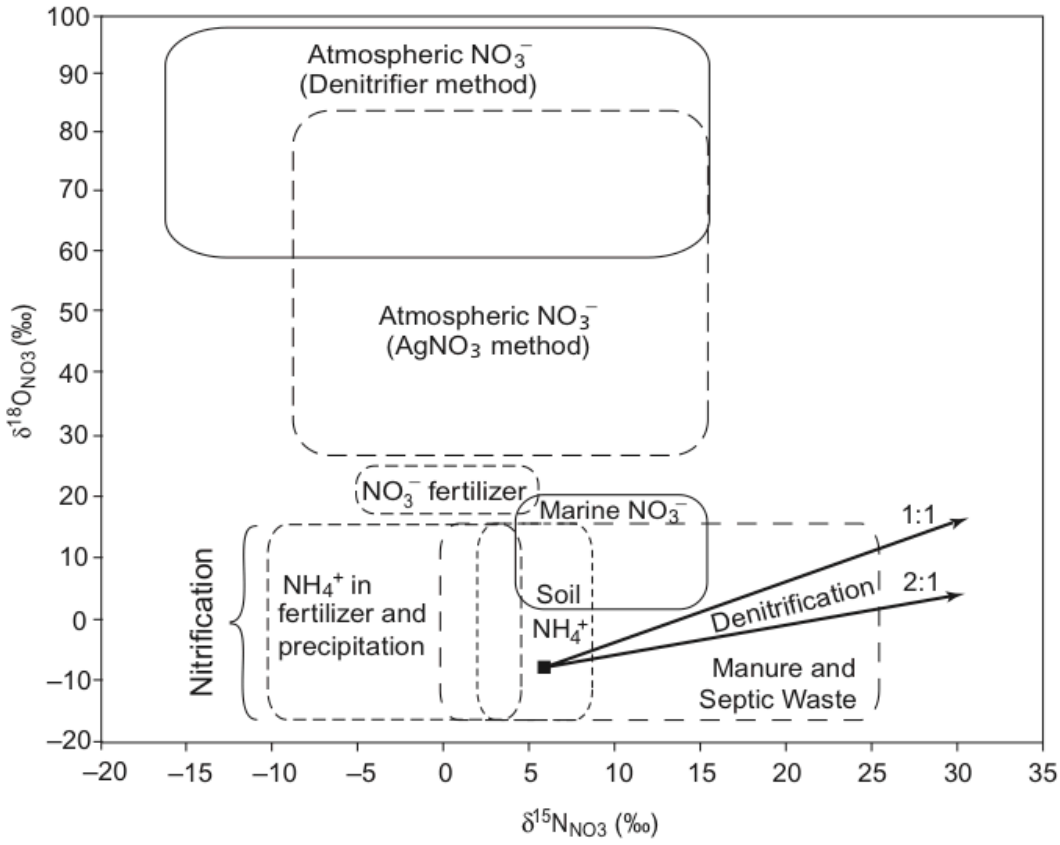

Figure 2.3 Kendall Plot showing $\delta^{18}O_{NO3}$ vs $\delta^{15}N_{NO3}$ and the categories for nitrate sources on the graph (Kendall et al. 2007).

Stable isotopes are a useful tool for the identification of nitrate sources to the environment, however when used alone they will provide only part of the picture. Attempts have been made using only the $\delta^{15}N$ of nitrate and others combing this with the $\delta^{18}O$ values of the nitrate. The aspects of the nitrogen cycle that nitrogen and oxygen isotopes of nitrate record are not exactly the same and so they can provide complimentary information (Casciotti et al. 2002). Bivariate $\delta^{15}N$ and $\delta^{18}O$ diagrams are also known as Kendall Plots (Figure 2.3). Such presentations provide an ability to interpret nitrate source contributions, however there is often a high level of overlap for in natural mixed source systems. Complimentary geochemical data, along with understanding of the hydrogeologic setting, is also required.

The isotopic composition of nitrogen in nitrate can be highly variable, ranging from $\delta^{15}N$ values of -10 to +25. The different isotopic compositions can represent different source so nitrate and can therefore be used for the identification of individual nitrate sources to water. In considering the sources of the nitrate, the wider nitrogen cycle must be kept in mind. Possible mixing of several nitrate sources as well as kinetic isotopic fractionation could affect the isotopic composition, making it difficult to determine the source using only $\delta^{15}N$, especially if there is more than one source. Most researchers agree that the combination of oxygen isotope data and other geochemical analysis with the nitrogen isotope data will provide more accurate interpretations of source contributions.

2.8.1. Uncontaminated Waters

Nitrate concentrations for groundwater uncontaminated by anthropogenic sources are generally low, usually below 1 mg/L (Hanson 2002) and within the range <0.05 – 25 mg/L nitrate-nitrogen. In rare instances higher concentrations may be present if recycling of buried plant matter is occurring (Seiler 2005). Uncontaminated groundwater has isotopic compositions that are comparable to soil derived nitrates as this is the primary source of natural nitrate. $\delta^{15}N$ values for soil nitrate are between -0.7 to +8‰ (Rock & Mayer 2002; Seiler 2005; Deutsch et al. 2006; Xue et al. 2009). The $\delta^{18}O$ values of nitrate for uncontaminated groundwater typically range between +0.5 to +2.7‰ (Rock & Mayer 2002; Deutsch et al. 2006).

2.8.2. Inorganic Fertiliser

Production of fertilisers is through the fixation of atmospheric nitrogen. This means that there should be little fractionation occurring and $\delta^{15}N$ value of the nitrate will be approximately -1.6‰ (Widory et al. 2004; Widory et al. 2005) with a usual range of -4 to +4‰. There has been some $\delta^{15}N$ values recorded in the range of -8 to +7‰ for fertilisers(Spruill et al. 2002; Kendall et al. 2007). The $\delta^{18}O$ values of the nitrate derived from fertilisers are expected to be

similar to the values for atmospheric O_2, of approximately +20‰ (Seiler 2005). In the literature, fertilisers have been observed to have $\delta^{18}O$ for nitrate in the range of +17 to +25‰ (Kendall et al. 2007).

2.8.3. Manure (Animal Waste)

Nitrogen in manure occurs as urea, which is then eventually converted to nitrate in the soil zone. This is done in three steps; the urea is first converted to NH_3 and then to NH_4^+. The NH_4^+ is left strongly enriched in ^{15}N as a result of ammonia volatilisation when NH_3 gas is lost during the conversion as well as equilibrium fractionation between ammonia and ammonium. The enriched NH_4^+ is then oxidised to nitrite and then nitrate via nitrification. $\delta^{15}N$ values of the nitrate are typically in the range of 10-20‰ (Kendall et al. 2007), though can have values which are much more positive than this. Using $\delta^{15}N$ values alone it is difficult if not impossible to distinguish human from other animal waste, however a multi-isotope approach has achieved this in the past (Kendall et al. 2007). The $\delta^{18}O$ values for the nitrate which is produced from urea range between +2 to +14‰ (Deutsch et al. 2006).

2.8.4. Industrial Wastewater

The range of $\delta^{15}N$ values in various forms of industrial wastewater is fairly large as the sources can be a variety of chemicals and waste material. The reported range of $\delta^{15}N$ values is +10.3 to +23.5‰ (Widory et al. 2005), however the range could be much greater as the global dataset is somewhat limited.

2.9. Micropollutants as Groundwater Tracers

Various micropollutants have been used as a way in which to identify the presence of and at times the source of contaminated water. Such information when coupled with geochemical and isotopic information can make source identification possible. This can be in the form of pharmaceuticals, hormones, herbicides, pesticides or other pollutants that are source specific.

When micropollutants are used as tracers a number of different traits are sought. These include the existence of the tracer at background levels and whether it is source specific, whether or not the tracer degrades over time and the minimum level of analytical detection at an acceptable level of precision for the tracer.

Chapter 3 - Canterbury Central Plains Geochemistry

3.1. Central Canterbury Plains Hydrogeology

Large-scale groundwater flow paths across the Canterbury region are relatively well understood. The groundwater flow direction is near perpendicular to the coast (Stewart et al. 2002) through aquifers which are sub-parallel to topography (Scott 1980). Recharge to the aquifers is spatially and temporally variable, from multiple recharge sources including rainfall, irrigation, infiltration from rivers, and snow melt. Further away from major rivers, rainfall becomes more significant as the source of recharge, while wells immediately adjacent to the rivers are recharged primarily by river water. Nearer to the coast, irrigation becomes a more prominent source of recharge to the aquifers, especially down gradient of the Ashburton-Lyndhurst Irrigation Scheme (ALIS). Recharge from irrigation has become more significant in recent years as the amount of irrigated land has become more widespread (Stewart et al. 2002).

Oxygen stable isotopes of water have been used in order to identify the contribution of each source to the groundwater. These data show that the recharge from rainfall varies from 7% adjacent to rivers, to 100% between rivers (Close et al. 1995). In areas where significant irrigation occurs, approximately 50% of water is contributed by rainfall and 50% from irrigation water (Close et al. 1995). The Close et al. study in 1995 and the Stewart et al. study in 2002 were compared revealing that near to the Ashburton River, recharge sources have remained very similar over the seven-year period. More negative $\delta^{18}O$ values were observed in 2002 than in 1995, suggesting an increase in the recharge from the ALIS relative to recharge from rainfall, as groundwater is ^{18}O depleted with local rain, highlighting the increasing effect of irrigation. Meanwhile, in the north, near the Rakaia River, there was little change in the groundwater $\delta^{18}O$ values (Stewart et al. 2002). Variation in recharge source

occurs seasonally and from year to year depending on rainfall. In years or seasons with higher rainfall, the rainfall becomes a more significant contributor to the groundwater, whereas in drier months or years the river and irrigation recharge, which are more stable and regular, are a greater percentage of the recharge (Close et al. 1995).

3.2. Central Canterbury Plains Water Sampling

Water samples were collected across the Central Canterbury Plains between 2010 and 2012. In total 191 groundwater samples were obtained from 35 wells and 25 surface water samples from 11 sites (Figure 3.1). The wells that were sampled ranged in depth from 6.5 to 95.6 metres, with a median well depth of 25 metres. Most groundwater samples were taken from between 20 and 50 metres depth. The choice of sample wells was the result of a variety of different factors, including availability of wells for sampling, aquifer depths, and a desire to sample shallower wells as these are more affected by nitrate pollution than deeper water. A full summary of results is provided in appendices one and two.

In the field, wells were first pumped to remove the standing water and to obtain a representative sample of the groundwater. Initially, samples were measured for temperature and pH, as well as an in field titration being completed to establish alkalinity. Samples of water were also collected for analysis of, δ^{13}C-DIC, and δ^{15}N and δ^{18}O isotopes of nitrate in water. Nitrate concentrations were determined on filtered (0.45 μm) samples, either using an in field colorimeter or a reagent free ion chromatograph (RF-IC) at the University of Canterbury. The samples analysed by the RF-IC were compared to in-field colorimeter measurements and a calibration curve was created to correct for drift in the colorimeter. δ^{13}C-DIC samples were analysed using the isotope ratio mass spectrometer at the University of Canterbury. A selection of surface water and groundwater samples also were analysed using isotope ratio mass spectrometry for the δ^{18}O and δD of water. Selected samples were

analysed for the nitrate isotopes of water using the bacterial denitrifier method at the United States Geological Survey (Sigman et al. 2001; Casciotti et al. 2002; McIlvin & Casciotti 2011) as outlined in chapter two. This method was chosen due to the ability to obtain both the $\delta^{15}N$ and the $\delta^{18}O$ values and the small water sample size that is required.

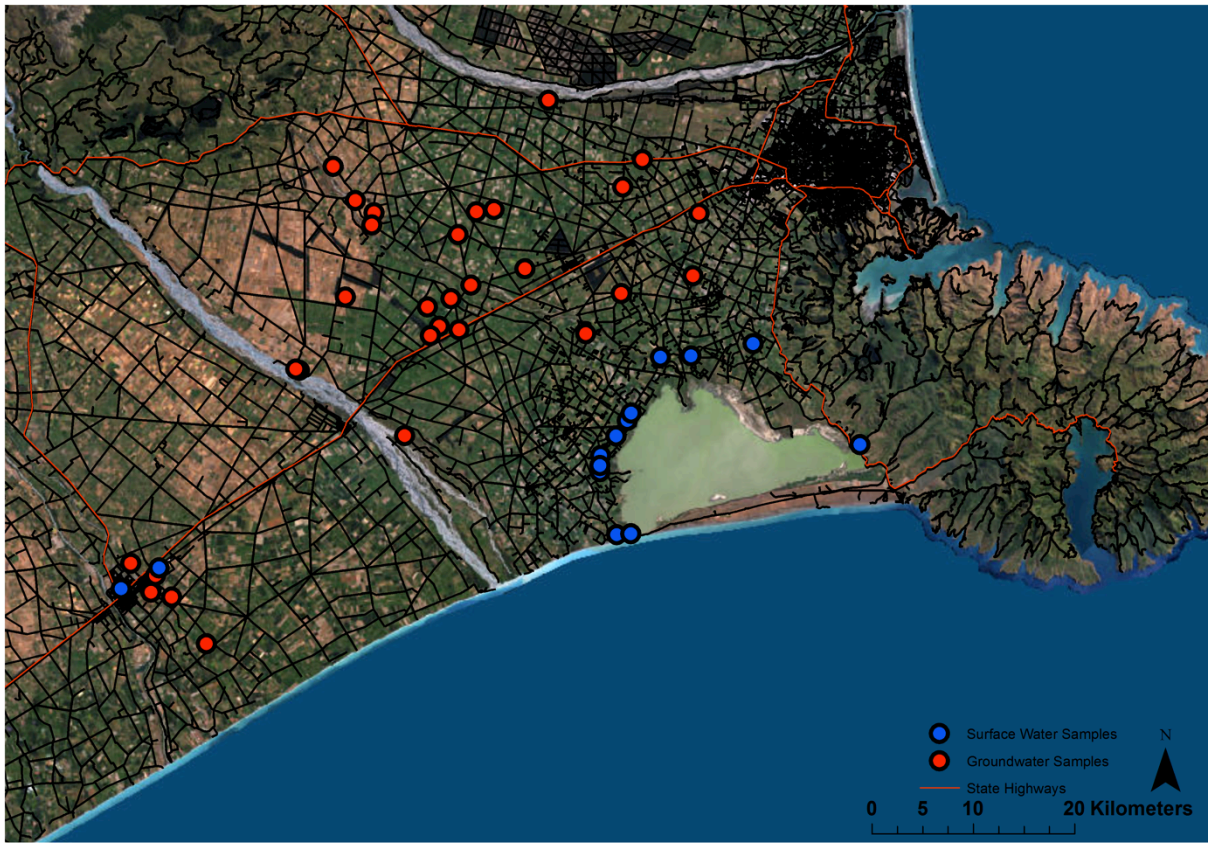

Figure 3.1 Groundwater and surface water sample site across the Central Canterbury Plains.

3.3. Canterbury Plains Nitrate

Several nitrate studies have been undertaken in the Canterbury region in the recent past (Close et al. 1995; Stewart et al. 2002; Hayward & Hanson 2004). The aquifers of the Canterbury Plains are at risk of contamination as land use changes and intensification. Unconfined and semi-confined aquifers are much more vulnerable to the effects of contamination from both past and present land uses than confined aquifers (Ford & Taylor 2006). An expected range of nitrate-nitrogen concentrations for the Rakaia-Ashburton Plains is now given as 4-12 mg/L. Such elevated nitrate concentrations have been present in water

as far back as 1950 and in wells as deep as 100 m or more (Stewart et al. 2002). The youngest water, which is recharged by rivers, tends to have the lowest concentrations of nitrate. It is likely from these trends that the nitrate concentrations in recent times are either remaining very similar or increasing slightly (Stewart et al. 2002). Nitrate entering the groundwater is likely transported through soils by rainfall recharge. Irrigation transports less water as it occurs during summer months when a larger portion of the water will be used for evapotranspiration, and therefore less water will remain to filter through the soil to the groundwater. Previous $\delta^{15}N$ isotope data reports values that cluster around +4 to +5‰, the typical values for soil nitrate, though it is suggested by Stewart et al. (2002) that cropping could be the nitrate source providing such values in Canterbury.

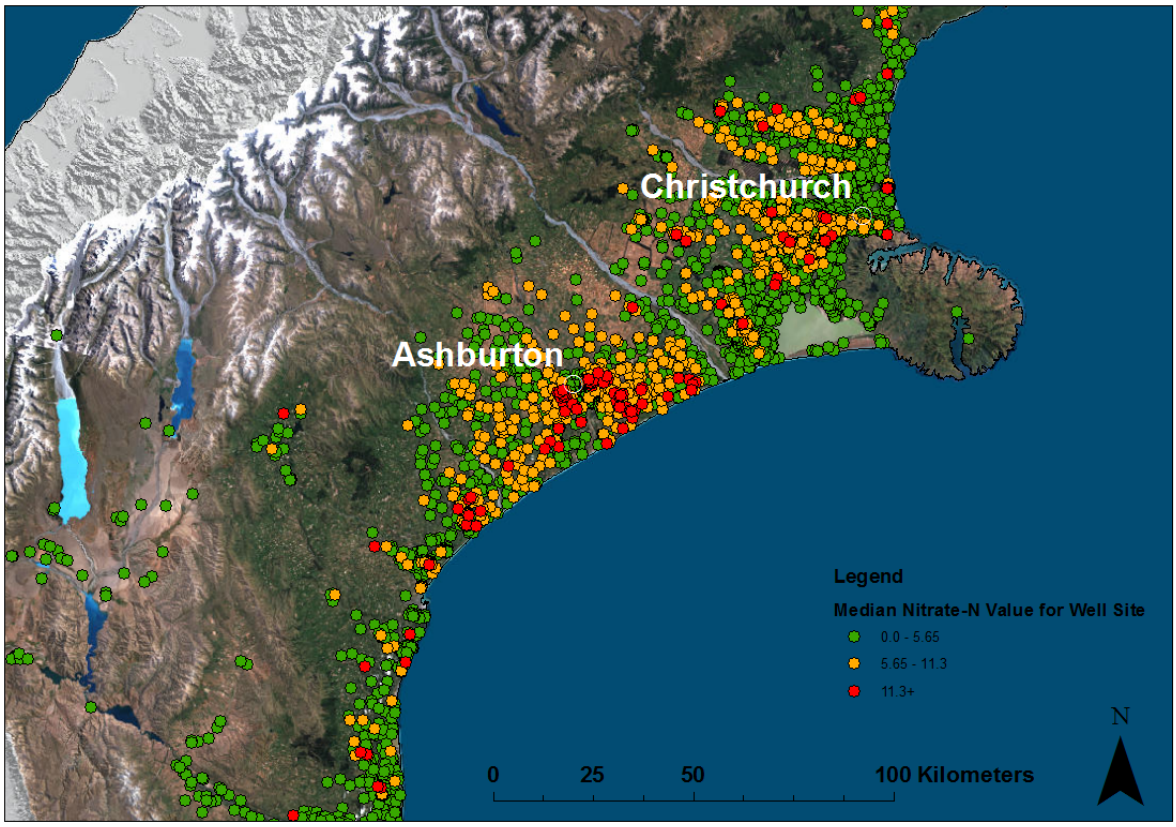

Figure 3.2 Median nitrate-nitrogen values for all wells sampled in the Canterbury region by Environment Canterbury. Data source: Environment Canterbury Wells Database.

Environment Canterbury records of nitrate concentrations extend as far back as 1954, however, regular regional surveys did not begin until the late 1970's (Hanson 2002). Data

prior to January 2011 was obtained from the Environment Canterbury database and nitrate concentrations up until this time were reviewed. The record includes 24,030 different samples taken from 3,498 sampling wells. For all wells the median nitrate-nitrogen value was calculated using every water quality sample at the site. Of these, 122 (3.5%) were found to have a median value higher than the MAV of 11.3 mg/l while a further 715 (20%) wells had a median value higher than 5.65 mg/l or half of the MAV.

There are some clear patterns in the distribution of nitrate contamination in Canterbury groundwater. These reflect both point sources and diffuse sources across the plains. Figure 3.2 shows the median nitrate-nitrogen values for all of the wells that have been sampled by Environment Canterbury since the first samples in 1954, through until samples from within the last year. At some sites there may only be one sample, while at others are represented by multiple, regularly collected, samples. Timing of sample collection was variable for different wells. However, despite these inconsistencies in sample timing and location, it is still possible to identify patterns in the distribution of nitrate in the groundwater. The figure uses red to show sites where the median nitrate-nitrogen is over the MAV of 11.3 mg/L, orange if the value is over half of this and green for those below 5.65 mg/L. Nitrate contamination occurs most frequently closer to the coast, suggesting an anthropogenic driver. The Central Canterbury Plains include a widespread area with nitrate values consistently above half of the MAV. There also appears to be an area of lower nitrate concentration bordering the major rivers, showing these areas are less contaminated, presumably due to the channel leakage and associated dilution effects. Sites that are above the MAV occur throughout the region and appear to be associated with local point sources or site-specific conditions.

The nitrate-nitrogen concentration of the samples collected for the Central Canterbury Plains as part of this study ranged from less than 1 mg/L to 24 mg/L, more than twice the MAV. The median nitrate concentration was 7.2 mg/L showing that while the nitrate overall might

not be at contaminated levels everywhere, it is generally above a natural background level and occurrences of extreme concentrations are present. Given the wide rang in concentrations it is perhaps likely that the groundwater is being polluted by either one or more anthropogenic sources across the Plains.

Nitrate-nitrogen concentrations have been gradually increasing since records began in 1954 (Figure 3.3). There was a peak in the annual median concentrations around 1980, before a decline in the early 1980's followed by a continued, on going gradual increase. This peak and decline in median nitrate concentrations may be the result of either changing management practices, especially around point source discharge of nitrate with the implementation of the Resource Management Act in 1991, or it may be attributable to the volume and spatial distribution of sampling that was carried out. The constant evolution of land use may also have an influence due to the relatively low transit time of groundwater in Canterbury. Since the mid 1990's regional sampling has been more widespread, with approximately 1000 samples collected per year. Prior to this, the number of samples collected in any given year varied greatly and sample sites varied from year to year. As a result averages for a particular year may be affected by where and when the sampling for that year was carried out. The median value given for 2011 is a result of samples from this study, and while being representative of a widespread area of Canterbury, there are not as many samples as in other recent years and the 2011 median may be higher than the actual median for all of the data over the entire region due to the focus on shallower wells.

Between the Rakaia and Ashburton rivers there is a widespread area of elevated nitrate values that could be the result of a series of different factors. These could to be related to the increase in dairy farming activity in this area. With the increase in farming there has been an increase in the fertiliser used on the land, more waste material from animals on farms,

increased irrigation of the land and a change in the vegetative cover. Other land uses, such as cropping have also become more intensive with the increase in irrigated land.

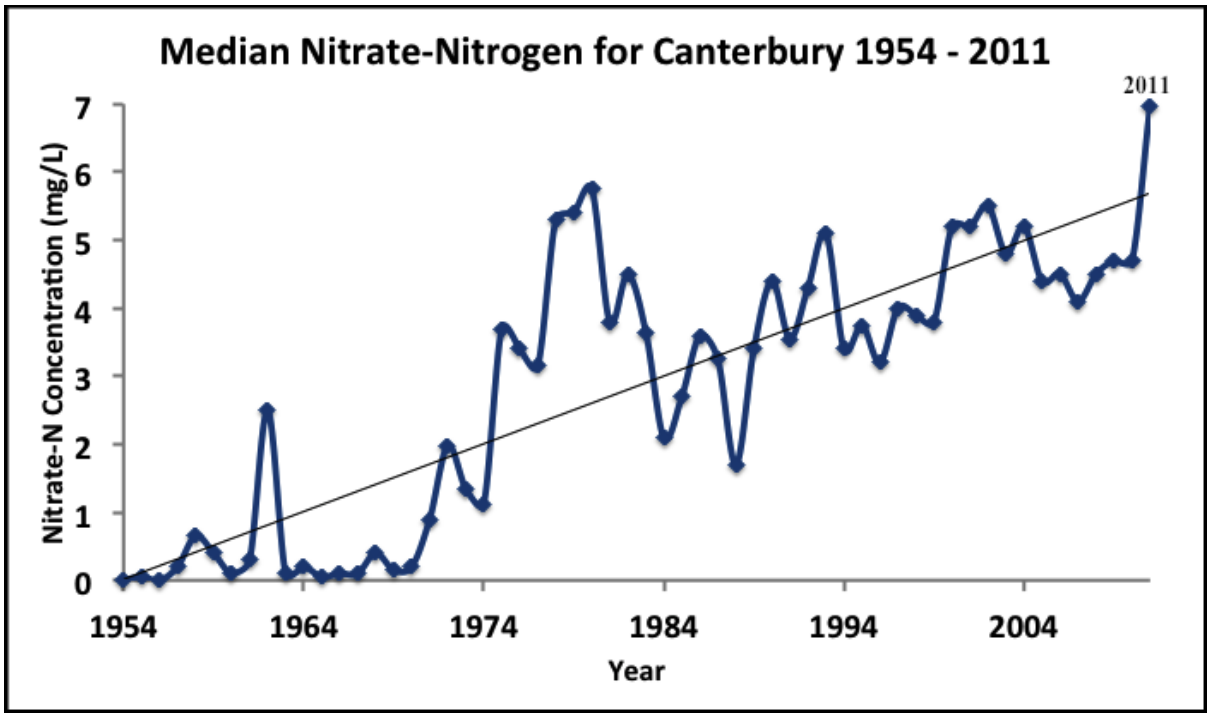

Figure 3.3 Annual median nitrate-nitrogen concentrations for Canterbury 1954-2011. Data up to 2010 sourced from the Environment Canterbury wells database. 2011 data represents this study.

Land use in Canterbury has changed significantly since early European settlement in the mid 1800's. This has led to a diverse range of land use types in the region, including mixed uses on individual farms. As discussed in chapter one, the last 30 years has seen acceleration in the switch to dairy farming. Dairy farming conversions have led to an increase in dairy cattle in Canterbury from 150,000 in 1994 to more than 700,000 in 2009 (Dynes et al. 2010). During this period, sheep numbers have dropped significantly. It is also important to note that in Canterbury the stocking rate in terms of cows per hectare is the highest in New Zealand at 3.28 cows per ha (Dynes et al. 2010), making dairy farming in the region even more intensive than the traditional dairy farming regions of Waikato and Taranaki (Pangborn & Woodford 2011). While dairy cattle numbers in Canterbury increased by 360% between 1994 and 2009 (Dynes et al. 2010), land use area for dairy farming increased by only 200% from 1995 to 2007 (Hill 2008), a clear demonstration of the intensified land use.

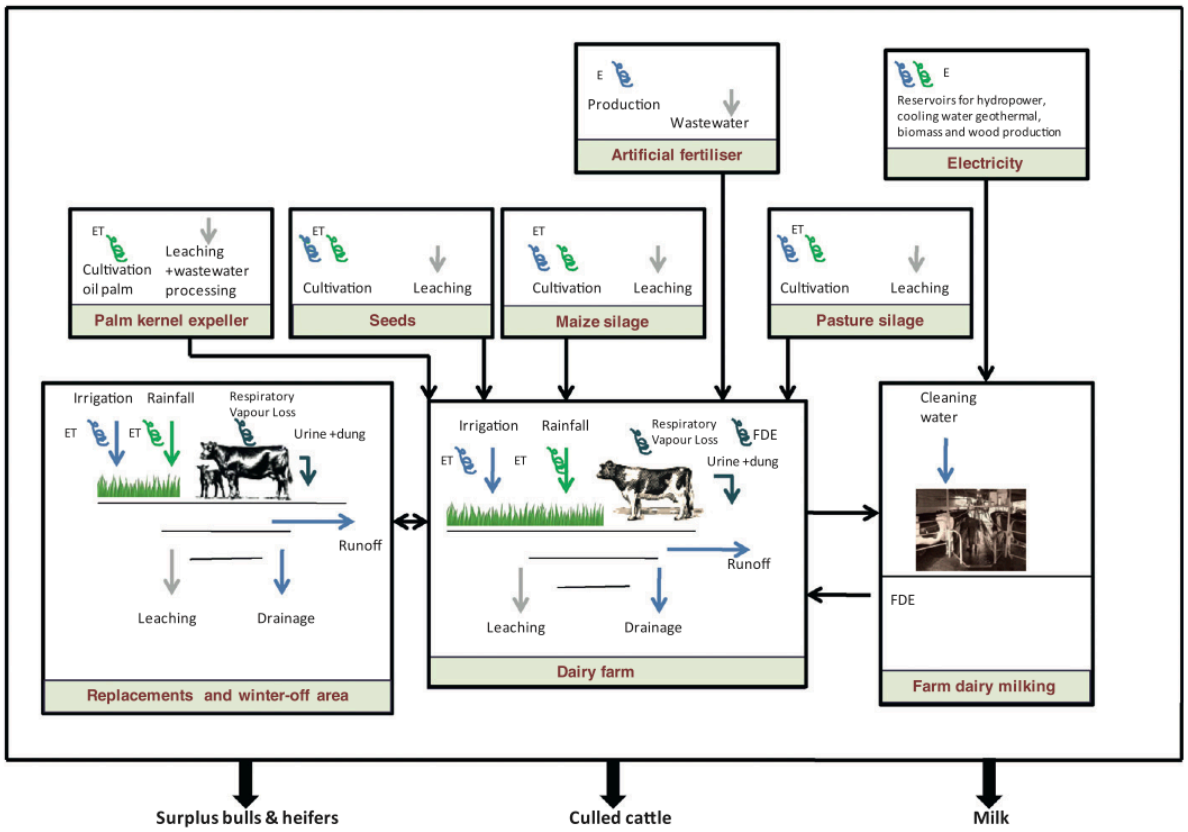

Figure 3.4 Life cycling in dairy farms of New Zealand (Zonderland-Thomassen & Ledgard 2012).

Fertiliser use in dairy farming regions of New Zealand has increased significantly as the demand for higher production has increased. Overall in New Zealand there was a 113 percent increase in fertiliser application between 1986 and 2002, with much of the increase attributable to the Canterbury region. By 2004 Canterbury had overtaken Waikato as New Zealand's heaviest user of fertiliser (Statistics New Zealand 2006). Most of the increase in fertiliser application in Canterbury has been in urea-based fertilisers. The application of these increased by 40% from 2002 to 2004 while there was a 5% decline in the application of lime fertiliser and a 32% increase in phosphorous fertilisers (Statistics New Zealand 2006). This is significant, as urea fertiliser contributes nitrogen to the soil and eventually the groundwater to varying degrees, whereas lime fertilisers only provide calcium, magnesium and dissolved carbonate ions to the soil.

In addition to the increase in fertiliser use, there has also been a change in land cover, with most New Zealand dairy farms containing a significant amount of clover in order to increase

the productivity as a clover dominated pasture is more nitrogen efficient than grass only systems (de Klein et al. 2010). Figure 3.4 demonstrates the nitrogen cycle in a manner more relevant to a dairy farm in New Zealand. Intensification sees the increase of all inputs into the system, including excreta, fertiliser, and biological fixation. Each of theses ahs the potential to increase the amount of nitrogen leached to surface water and groundwater bodies.

Canterbury has also seen an increase in the area of land irrigated, a near necessity in the arid Canterbury Plains system. In 1985, 150,000 ha of land in Canterbury was irrigated (Ford & Taylor 2006), by 2006 this was estimated to have reached 400,000 ha (Pangborn & Woodford 2011), and increase of 167%. Irrigation, fertilisation, or land receiving high rainfall, will also contribute to more nitrogen leaching to groundwater than in non-irrigated locations. The extent of nitrogen leaching also depends on the source of the nitrogen that is being applied to the land. Urine and dung are localised and highly concentrated in nitrogen, and when large amounts of water are applied, this nitrogen is leached to the groundwater at elevated concentrations (Pakrou & Dillon 2004). Alternatively, dairy shed effluent and fertilisers are spread more thinly over wider areas. This means that while water will carry nitrogen in various forms to the groundwater, it will be more dilute and more widespread.

There are two main methods of irrigation used in Canterbury, spray systems and flood irrigation. Prior to the year 2000 flood irrigation was significantly more common than the spray systems, however now some 80% of the irrigated farms use spray pivots (Dynes et al. 2010). Each of these systems influences the leaching of nitrogen to groundwater in different ways. Spray irrigation is much more efficient in its use of water and therefore places less pressure on groundwater resources. Only the water that is necessary is added and so less is wasted. There is however evidence to suggest that flood irrigation leads to lower concentrations of nitrate leaching into the groundwater (Di et al. 1998). Three main reasons are given for this including, the greater amount of water in flood irrigation dilutes the nitrate,

there is greater loss of nitrogen as a result of denitrification due to wetter soils, and there is a more significant bypass flow (Di et al. 1998). In a spray irrigation system, less dilution and less denitrification occur, so more nitrate is leached to the groundwater. However, this can be altered by water accumulating with application over a long period of time.

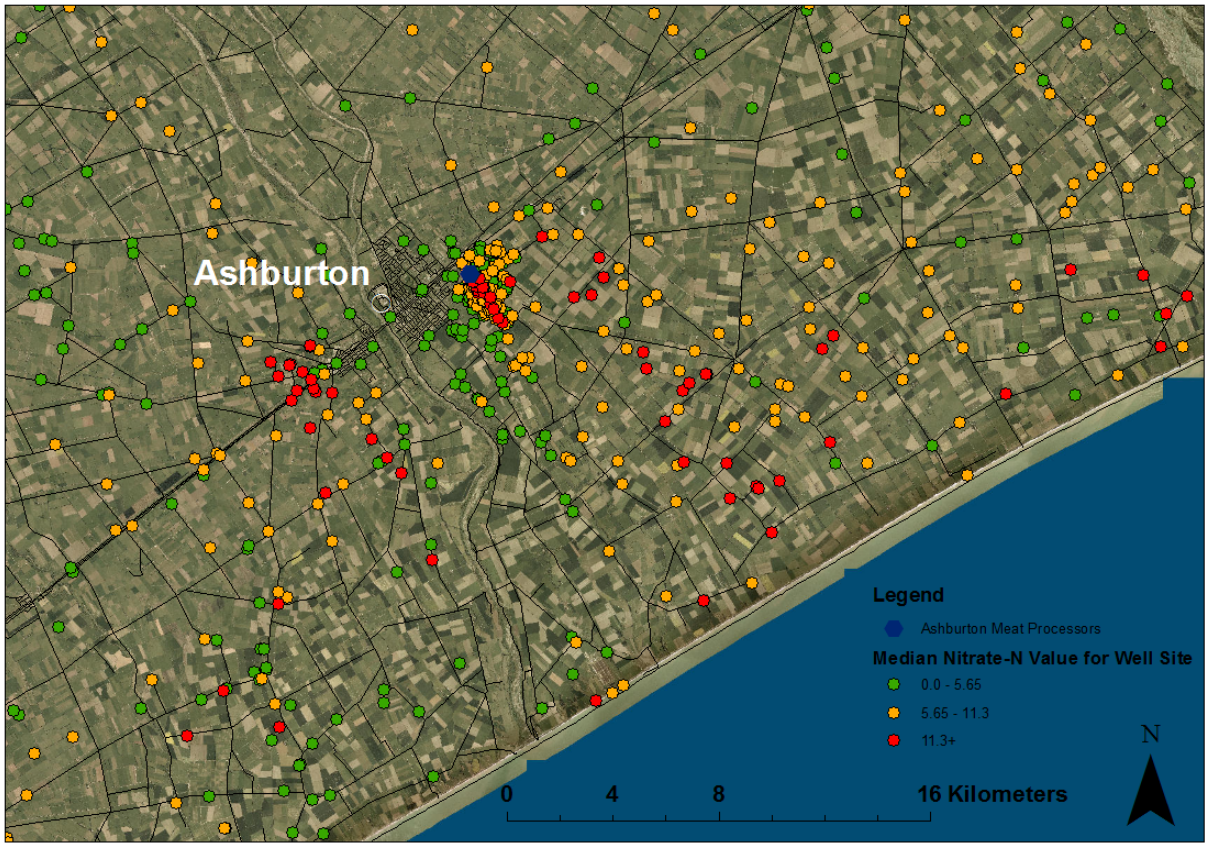

Figure 3.5 Median nitrate-nitrogen for all samples taken from groundwater wells in the Ashburton area. Data sourced from the Environment Canterbury Wells Database

Figure 3.5 shows the same data as figure 3.2, with a particular focus on the Ashburton area. The patterns of the larger scale are reflected, with a significant area of high nitrate-nitrogen values across the coastal plains, an area of lower concentrations bordering the Ashburton River and the more extreme values that exceed the MAV associated with point sources.

The Ashburton Meat Processing plant is shown on the map and there is a clear plume of nitrate that exceeds the MAV extending towards the southeast of the plant, parallel to the groundwater flow direction. The concentrations seen down gradient of AMP are not observed

up gradient of the plant, suggesting an association with the waste that has been deposited at the AMP site. Towards the northeast and east of this plume there are further zones of wells that have median concentrations above the MAV. These areas of nitrate concentration can be correlated with two other meat-processing plants that have also been depositing waste in the area. Near the southern boundary of Ashburton a further area of high nitrate concentration in groundwater is seen. The source of this nitrate is not as clear in this area as the other contaminated zones. There could be some older domestic septic systems in the area that are not well maintained, or a nearby golf course may also be affecting groundwater quality in the area through fertiliser use.

The Ashburton area nitrate concentrations also suggest that the Ashburton River is losing water to the groundwater system. Lower nitrate values form a band along both sides of the river, suggesting that there is a flow of 'cleaner' water is entering the groundwater and flushing out contaminated water.

3.4. Nitrate Concentration and Depth

Correlations between nitrate concentrations and the depth of the sample well are clearly present. Generally, more contamination is seen is shallower wells, as nitrates leaching to the groundwater will flow through these first. This top-down pattern of nitrate contamination is almost certain evidence of a link between nitrate contamination of groundwater and human behaviours.

Nitrate concentrations in relation to depth for every nitrate sample in the Environment Canterbury wells database is shown in figure 3.6. A general decline in nitrate concentrations with increasing depth is clearly shown, with a marked decline in nitrate concentrations below 45 metres depth. Elevated nitrate concentrations at approximately 30-45 metres depth could

reflect the land use activity at the recharge point for the groundwater, showing a lateral transport pattern related to indirect recharge.

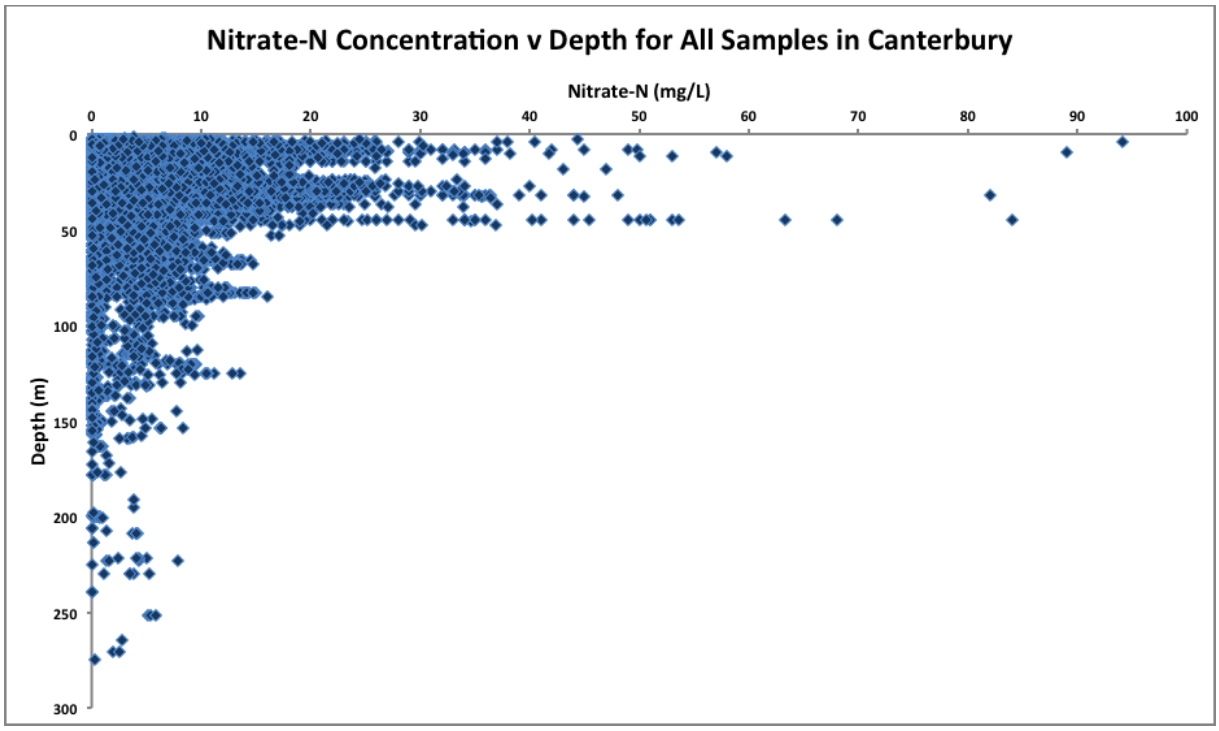

Figure 3.7 Nitrate-nitrogen concentrations in relation to depth across the whole Canterbury region. Data sourced from the Environment Canterbury wells database.

The significant decline in concentrations below 45 metres is important and there are a number of different explanations. Firstly, it may give an indication as to the rate in which water is filtering down through the various layers to deeper aquifers and therefore highlights when an increase in the nitrate being deposited on the land occurred. It may also suggest that interaction between waters above and below 45 metres is limited or restricted, possibly due to the presence of a lower permeability confining layer that separates them. The contamination that is therefore observed below this depth would be the result of either, a limited amount of nitrate moving through a low permeability zone, or nitrate entering the aquifer as a result of contamination at its recharge area, up gradient in the inland Canterbury Plains.

It is also worth noting the few extreme nitrate concentrations, above 40 mg/L nitrate-nitrogen in wells shallower than 10 metres. These are some of the highest concentrations ever

observed anywhere on the planet at any time. A likely reason for these extreme concentrations is that recharge from rivers as well as rainfall and irrigation means that water moves more rapidly through the shallow groundwater and so contaminated water is flushed out of the soil and shallow groundwater. It is likely in periods of higher river flow or significant rainfall that the nitrate in shallow groundwater may be briefly diluted by the addition of water.

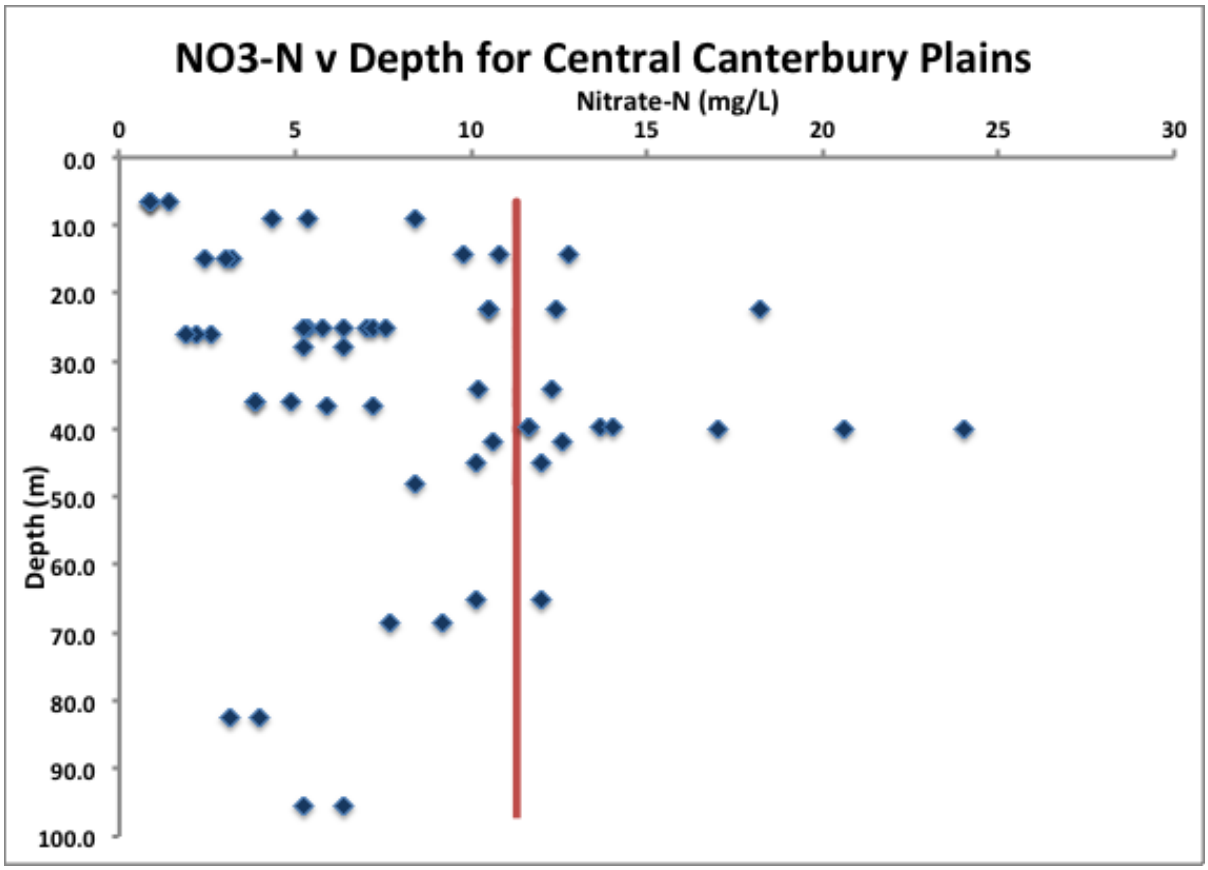

Figure 3.7 Nitrate-nitrogen concentrations in relation to the depth of wells across the Central Canterbury Plains.

Nitrate concentration at depths was also evaluated for the samples taken across the Central Canterbury Plains from 2010 to 2011. The results are shown in figure 3.7. Here patterns are not as pronounced as that of the Environment Canterbury data. There is a peak in concentrations at around 40 metres depth and a steady decline at increasing depths, thought this decline is not as distinct as the Environment Canterbury data. There is a large variability in concentrations in wells shallower than 45 metres, where the standard deviation is 5.0

around a median of 6.4 mg/L. Deeper than this the concentrations are generally lower, though often still above the background levels of approximately 4 mg/L.

Figure 3.7 suggests that there is at least some form of nitrate pollution occurring at all depths across the Central Canterbury Plains. Even the deepest well at over 95 metres depth contains nitrate concentrations of more than half the MAV and well above background levels. Contamination to greater depth is also seen in the data for all of Canterbury (Figure 3.6), where the concentrations reach more than half of the MAV at 295 metres deep, including a deep bore located near Darfield that exceeds the MAV (Potter, pers comm.).

3.5. Nitrate Concentration and Distance to Rivers

In figures 3.2 and 3.4 there are areas of low nitrate-nitrogen concentration bordering the major rivers. This suggests that the loss of water from the rivers to the groundwater is diluting any nitrate contaminating these areas. It is also likely that groundwater may be flowing more quickly through these parts, therefore any nitrate in the water will move through and not reside in the groundwater for a long period of time or accumulate.

Depth is also important for establishing the effects of the river water that is lost to the groundwater. This is demonstrated in figure 3.8, which shows the concentrations of nitrate-nitrogen at different distances from rivers and the depths for each of these. There is a zone of low nitrate-nitrogen concentrations to a depth of about 30 metres and 3.2 kilometres away from the rivers. This suggests that over the Central Canterbury Plains, the Waimakariri, Selwyn and Rakaia Rivers are losing water to at least this depth and distance. At further distances, and higher depths, concentrations are regularly over half of the MAV and occasionally above the MAV, suggesting little direct influence from the rivers in these areas. This could be due to a lack of connectivity of aquifers, a result of the flow path directions of groundwater, or the river water becoming contaminated once it interacts with the

groundwater further from the river. This general pattern of channel leakage agrees with previous research using oxygen isotopes to identify the sources of Canterbury groundwater (Stewart et al. 2002), including: the alpine rivers, rainfall, irrigation water. Nearer the rivers it is clear from the water isotopes that the rivers are the dominant source to groundwater, while further away it is similarly clear that irrigation and rainfall are more dominant sources. The nitrate concentrations in this study reinforce this interpretation.

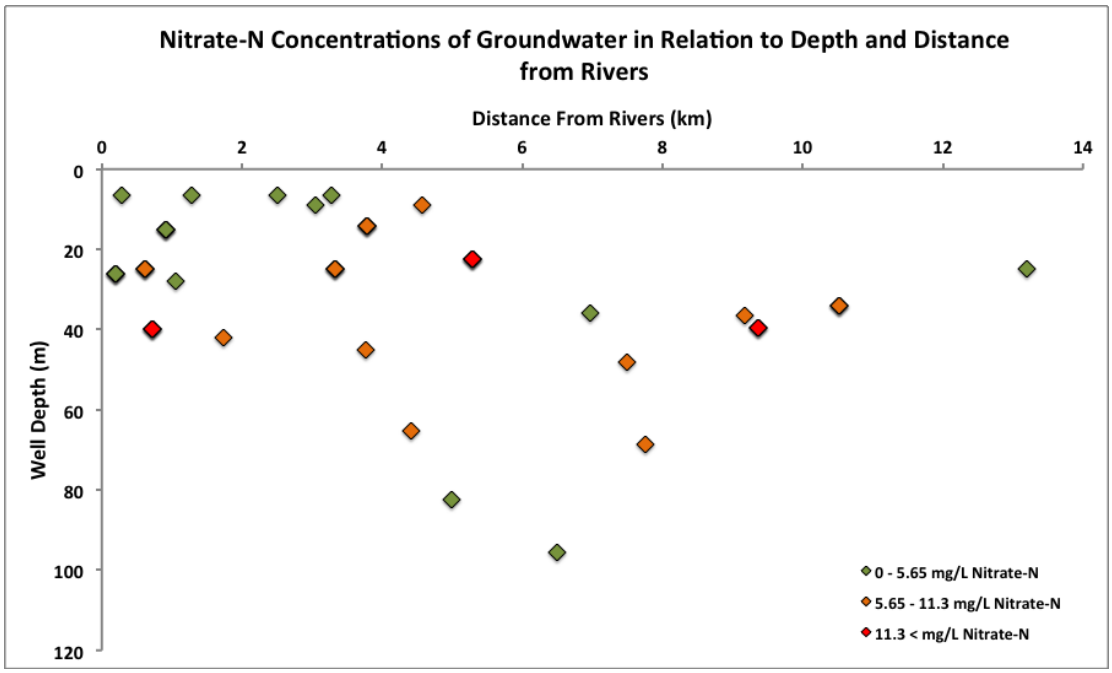

Figure 3.8 Nitrate-nitrogen concentrations of groundwater in the Central Canterbury Plains in relation to depth and distance from rivers.

3.6. Other Anion Data

3.6.1. Bicarbonate (Alkalinity)

Alkalinity is predominantly the result of the amount inorganic carbon ions in the groundwater and provides a measurement of the bicarbonate and carbonate concentration. In the near neutral conditions of Canterbury, the main contributor to alkalinity is bicarbonate. The assumption is therefore made that alkalinity represents bicarbonate concentration (Hanson & Abraham 2009).

Figure 3.9 shows the alkalinity data collected for the Central Canterbury Plains during this study. The estimated values for biogenic carbon, the Waimakariri River, and rainfall recharge are also plotted (Stewart 2012). As water from the alpine rivers moves into the groundwater system, there will likely be an increase in the DIC concentration due to oxidation of organic matter. This organic matter may originate from the river bed or the river source and be carried by the river (Taylor & Fox 1996), or it may be obtained from interactions with the soil and aquifer. The Central Canterbury Plains data in figure 3.9 plots below the line that connects biogenic carbon and the alpine river. This demonstrates that there is contribution from both the alpine rivers and rainfall to the groundwater. Both sources are able to gain DIC through the oxidation of biogenic carbon (Stewart 2012), thus pulling data points further to the left in figure 3.9.

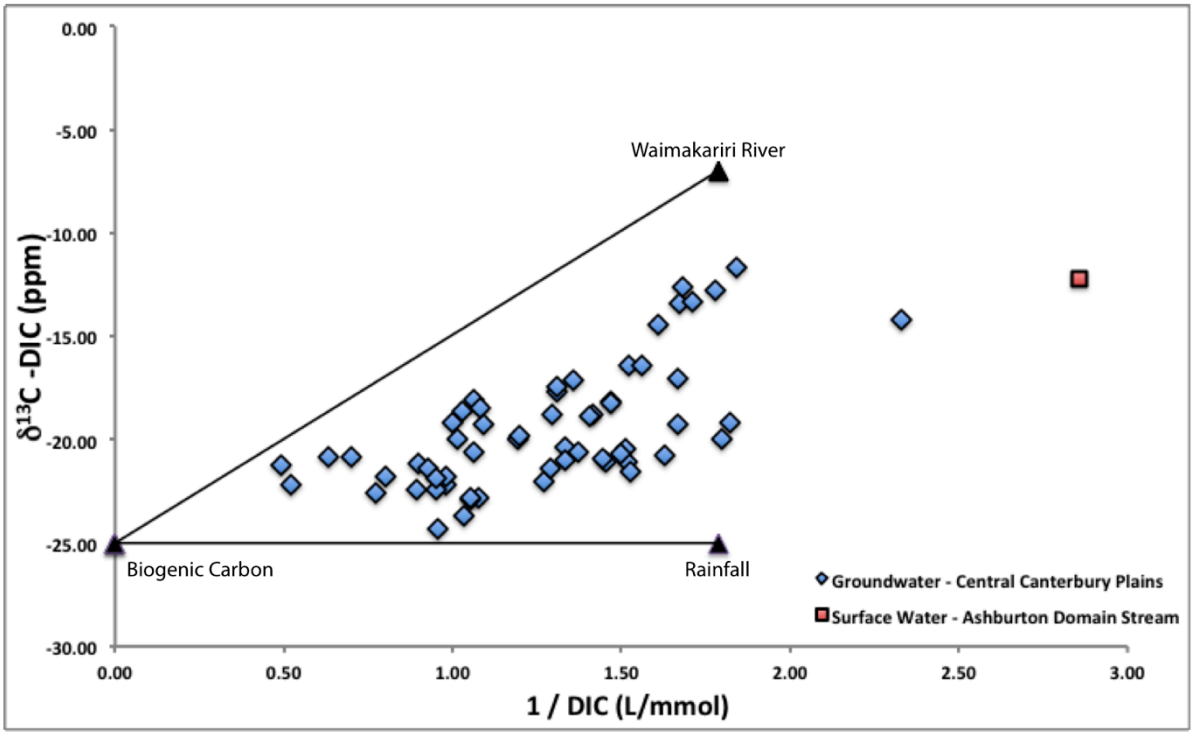

Figure 3.9 $\delta^{13}C$ vs 1/DIC plots for groundwater and surface water samples taken across the Central Canterbury Plains and near Ashburton in 2010 and 2011. Plot includes points representing values for the Waimakariri River, biogenic carbon and rainfall recharge (from, Stewart 2012).

3.6.2. Chloride

Chloride can also be an indicator of groundwater pollution or contamination and is often used in conjunction with nitrate concentrations to establish whether water has been contaminated. However, chloride is not known to have the detrimental effects on humans that are associated with nitrate. As a result there is no need for guidelines as to the concentration of chloride acceptable for drinking water. However, if the concentration is above 250 mg/L then there may be a detectable taste in the water, though people drinking this can become used to it (World Health Organisation 2003; Jain 2005). Sources of chloride to surface and groundwater are many and varied, including inorganic fertilisers, leaching from landfills, effluent from septic waste, industrial wastewater, drainage from irrigation, and saltwater intrusion. Natural levels of chloride in groundwater can vary significantly, especially in coastal areas where saltwater intrusion may have an effect on the groundwater. Chloride concentrations in waters that are considered to be unpolluted are generally below 10 mg/L, though concentrations are often lower than 1 mg/L (World Health Organisation 2003).

Environment Canterbury has records of chloride concentrations dating back to 1950. In total there are 22,776 measurements of chloride concentrations taken from 3,268 different groundwater sites. Of these, only 290 samples across 58 different wells contained taste detectable concentrations of chloride over 250 mg/L. The highest concentration of 16 500 mg/L was recorded in 1991 at Kaitorete Spit which separates Lake Ellesmere and the sea, a location where elevated chloride would be expected to occur naturally in shallow wells due to salt water intrusion.

The median concentration of chloride for all wells that have been sampled in Canterbury are shown is figure 3.10. The wells shown may be represented by only one sample, or may have over 200 samples, however the overall pattern and trend of chloride concentrations is still reliably demonstrated by the figure. It shows widespread areas where the concentration is

below 10 mg/L and therefore probably uncontaminated by chloride, while a vast majority of the region has medians below the taste detectable limit of 250 mg/L. Much higher chloride concentrations are generally seen nearer the coast, where either contaminated water has flowed through the groundwater on the inland plains, or salt-water intrusion from the sea is naturally elevating the chloride concentrations. Parts of the patterns in the nitrate data in figure 3.2 are replicated by figure 3.10 of the chloride data. The loss of water from rivers to groundwater is apparent again by the much lower concentrations of chloride in a band bordering either side of the major rivers. When plotted against depth, chloride concentrations show very few records of extreme values below 65 metres.

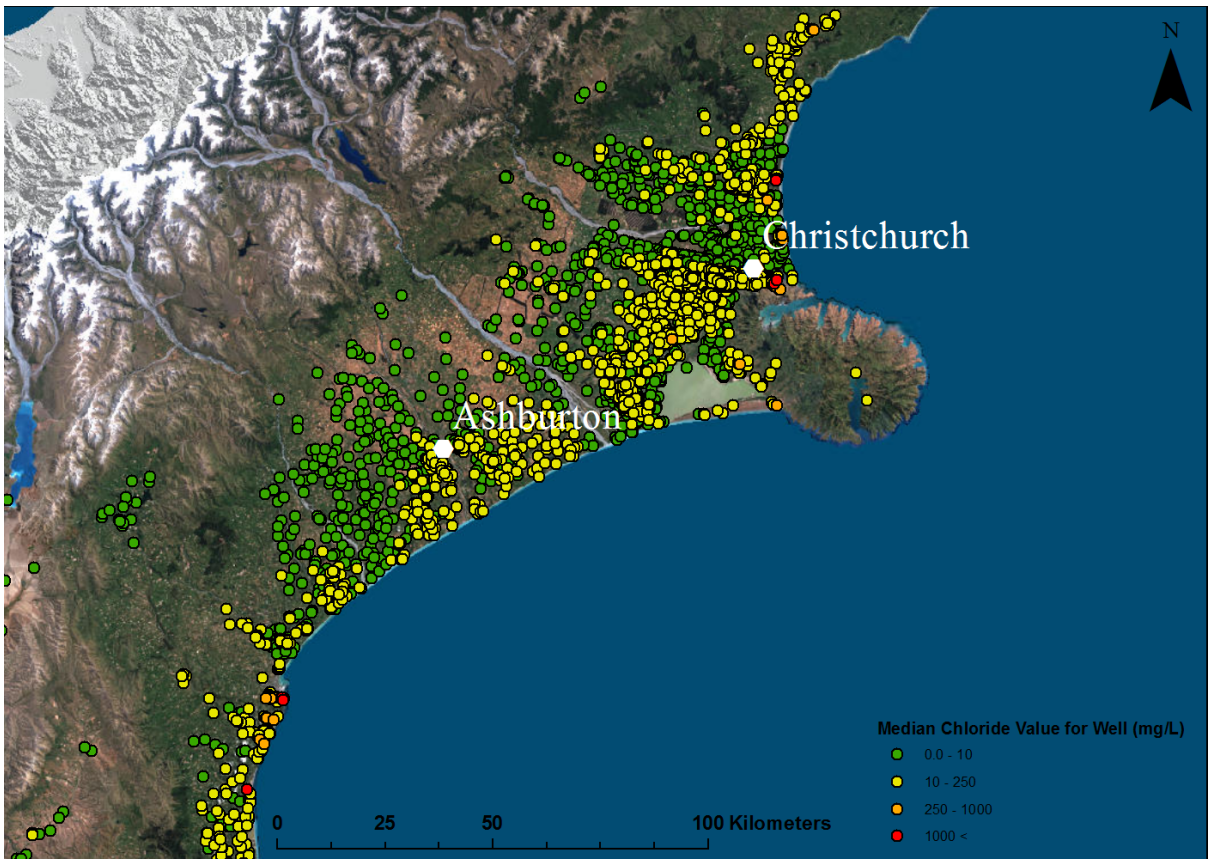

Figure 3.10 Median chloride concentrations for all wells in Canterbury. Data sourced from the Environment Canterbury wells database.

3.7. Canterbury Groundwater Nitrate in a Global Context

The issue of groundwater contamination by nitrate is not restricted to Canterbury or New Zealand. Many other locations in the world face similar challenges and are using a varying

degree of management practices. Of significant concern however, is that Canterbury's problem is comparable, if not more severe, than other locations worldwide. High nitrate values recorded in Canterbury are among some of the highest in the world when compared to other studies undertaken on nitrate contamination of groundwater. A selection of different studies that have been carried out in other regions is shown in figure 3.11, including some comparably agriculturally intensive regions, and the mean, median and maximum nitrate concentrations measured in each location.

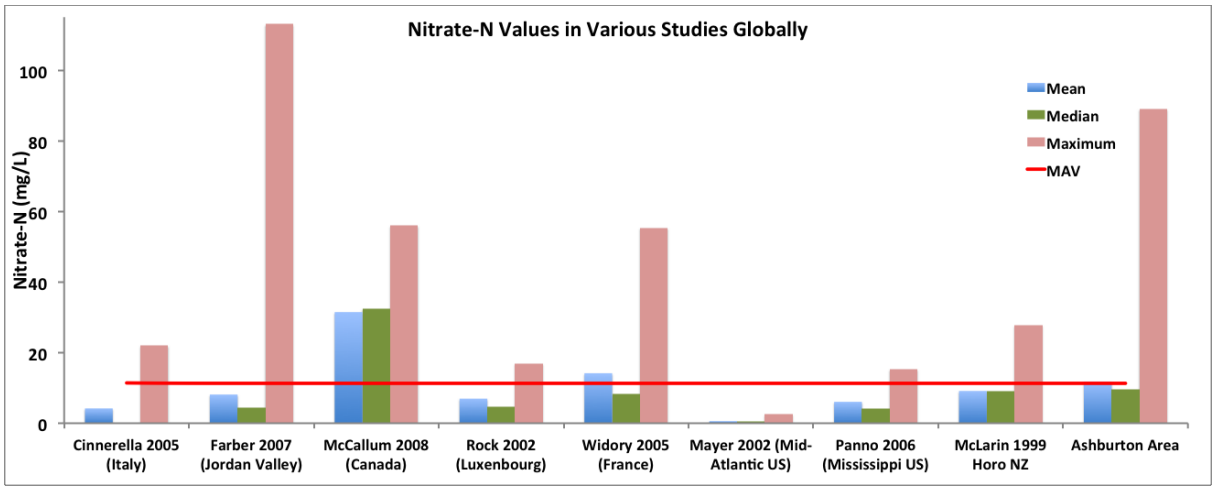

Figure 3.11 Nitrate-nitrogen concentrations as recorded by various studies around the world. Compared with data from the Environment Canterbury wells database (McLarin et al. 1999; Mayer et al. 2002; Rock & Mayer 2002; Cinnirella et al. 2005; Widory et al. 2005; Panno et al. 2006; Farber et al. 2007; McCallum et al. 2008).

These studies show a wide range of nitrate contamination over a variety of spatial and temporal scales. Only one of the studies examined here had a maximum nitrate concentration higher than the highest seen in the Environment Canterbury data. This was from a study in the Jordan Valley, between two very salt rich and evaporated seas, the Sea of Galilee and the Dead Sea. In Jordan, the elevated nitrate concentrations are the result of deep brines and not anthropogenic contamination (Farber et al. 2007). The study from Canada (McCallum et al. 2008) was undertaken on a manured field and all samples were from a depth of 3-4 metres. As a result the median, mean, and maximum show very high concentrations of nitrate. In France, the study (Widory et al. 2004; Widory et al. 2005) was widespread and covered a

number of settings as well as a number of nitrate sources. It is therefore in many respects similar to Canterbury and the results are comparable, and noticeably lower, than the data from around the Ashburton area. The only other New Zealand setting was in the Horowhenua (McLarin et al. 1999), in an area around the town of Manakau where dairy farming, market gardens and septic tanks all contribute nitrate to the groundwater and the nitrate concentrations are very similar to those of Canterbury.

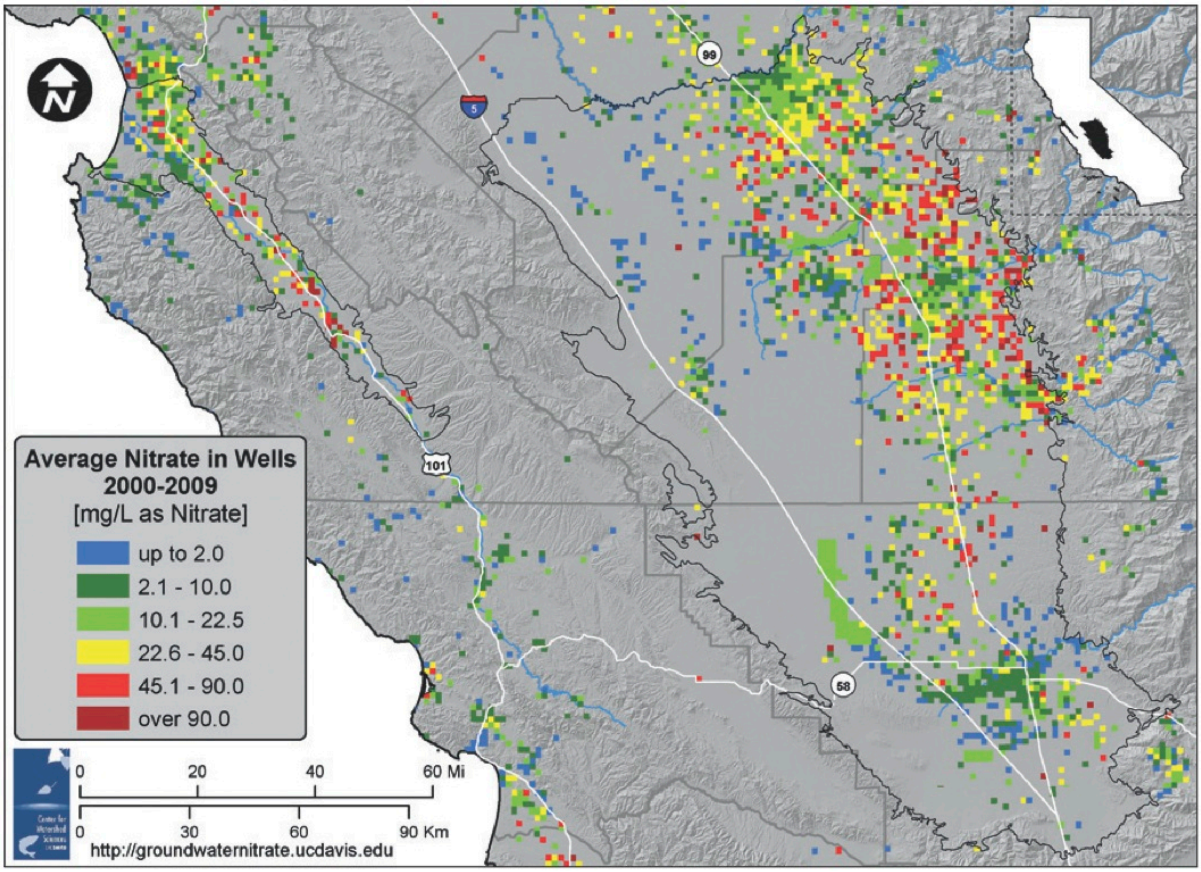

Figure 3.12 Mean of the time average nitrate concentration (mg/L) in each well belonging within a square mile land section, 2000-2009 in the Tulare Lake Basin and Salinas Valley (Harter & Lund 2012).

A region very similar to Canterbury in its size and land use is the Tulare Lake Basin and the Salinas Valley, California in the United States of America. In this region groundwater is an essential resource for agriculture, industry and urban use. There are also comparable challenges with nitrate contamination of the groundwater. Figure 3.12 of average nitrate concentrations in the Salinas Valley groundwater bears many resemblances to figure 3.2 in the frequency and distribution of different nitrate concentrations. Nitrate in this area of

California comes largely from agricultural waste and fertiliser, with other contributions significant in localised areas. An extensive report was prepared by the University of California, Davis (Harter & Lund 2012) and outlines the issues faced as well as suggesting possible methods of addressing the problems.

The report recognises the extreme economic cost that would be associated with large-scale reduction of nitrate inputs into the groundwater systems and instead focuses on the treatment of already contaminated water for subsequent use. Direct remediation of the groundwater in large aquifers is far too costly to implement, estimated to be in the order of US$13 to 30 billion. Methods of nitrate remediation include mixing contaminated water with clean water to lower nitrate concentrations to levels acceptable for drinking, or using an alternate water source. Funding of any remediation would be achieved through placing a fee on the key sources of nitrate to groundwater, such as fertiliser. A fee such as this would require evidence as to what sources are contributing more nitrate to the groundwater. Similar steps may be required in Canterbury in the near future with the on going increase in nitrate concentrations in regional groundwater in what is one of, if not the most sever example of nitrate contamination on the planet. In order to implement such measures in Canterbury there must be a comprehensive understanding as to the contribution of various sources. The spatial extent and economic significance are comparable to the above California example, making this USA case a potential source if information applicable to the Canterbury nitrate problem.

3.8. Isotopes of Water in Canterbury

Plotting surface water and groundwater δD and $\delta^{18}O$ (data in Appendix one) from the Central Canterbury Plains (Figure 3.13), shows that the two water types are distinguishable, with only a small overlap. Both plot near the global meteoric water line (GMWL), and form a local meteoric water line (LMWL) that has a similar slope (6.4). The LMWL established has

an r^2 value of 0.92 with little divergence from the trend in the data. Surface water of the Central Canterbury Plains water appears to be isotopically more negative than adjacent groundwater. This spread suggests that the surface water samples taken are being fed from more inland higher altitude meteoric water.

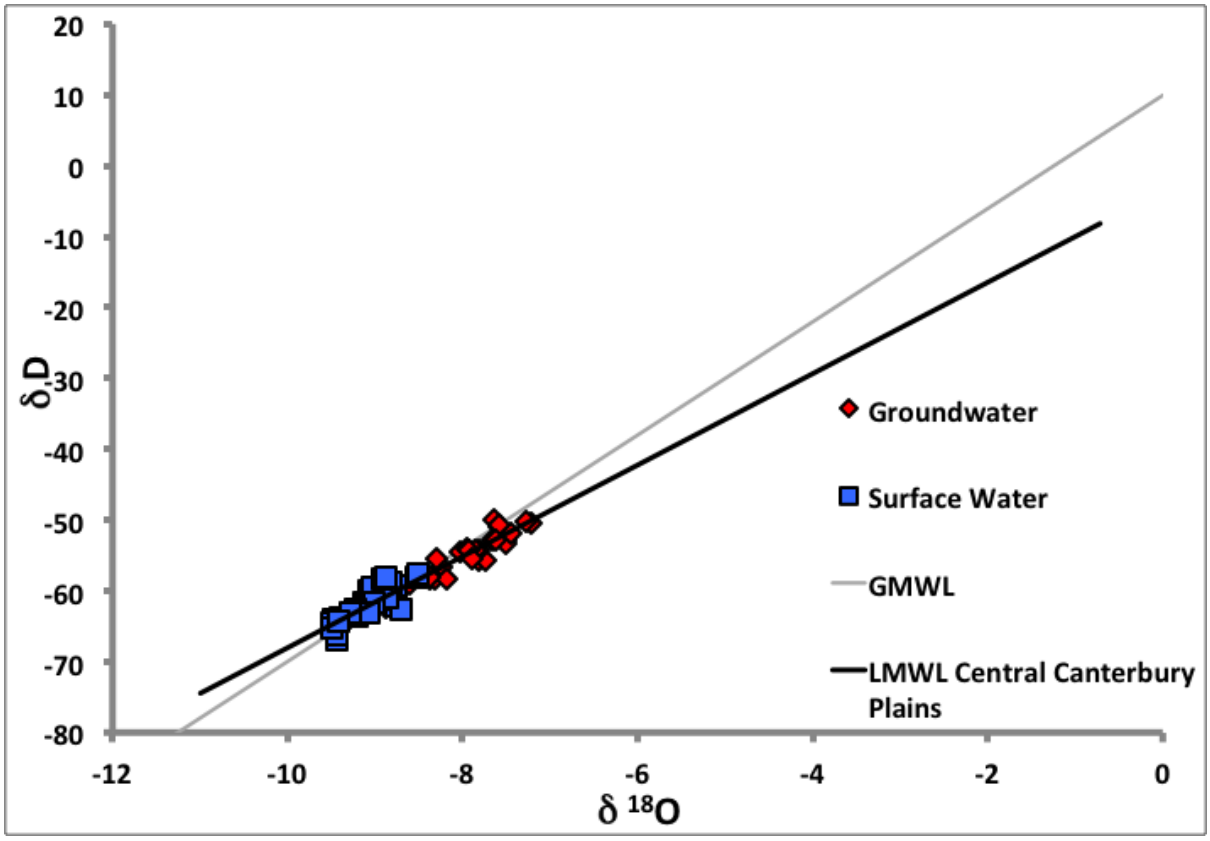

Figure 3.13 δD v δ^{18}O plot for water of the Central Canterbury Plains.

3.9. Nitrate Isotopes of Water of Canterbury

Studies of the nitrate isotopes in Canterbury, or other locations in New Zealand are limited and have yielded little in terms of identifying nitrate sources to the water. Figure 3.14 shows the δ^{18}O and δ^{15}N values of nitrate for groundwater data from the Central Canterbury Plains collected for this study, as well as surface water analysis in this study, and another recent study of streams on Banks Peninsula (Stewart 2011). Groundwater isotopes all plot between +1.95‰ and +6.68‰ δ^{15}N and -2‰ and +4.4‰ δ^{18}O, which is in the expected range for naturally occurring soil nitrate (Kendall et al. 2007). The surface water has a more diverse

range of isotopic compositions. Much of the spread of the data is a result of including the Banks Peninsula stream dataset. The Banks Peninsula data was collected from a series of streams spanning distinct land use classes. Nitrate concentrations recorded on Banks Peninsula ranged from <0.001 to 2.5 mg/L (Stewart 2011), much lower than most of the surface water of the Central Canterbury Plains, which was observed in this study to range between 0.6 and 11.4 mg/L.

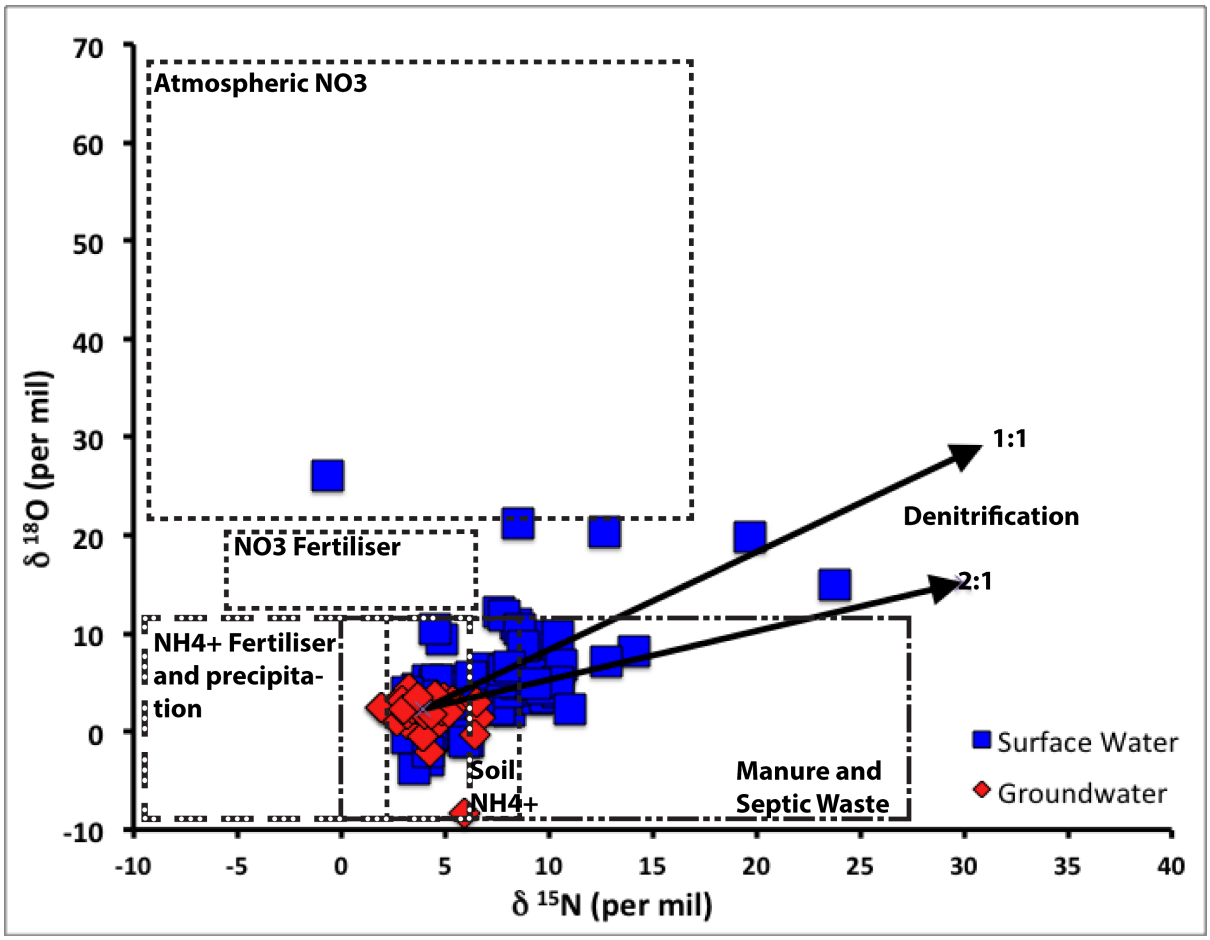

Figure 3.14 $\delta^{15}N$ v $\delta^{18}O$ plot for groundwater and surface water of the Central Canterbury Plains in 2011 and the surface water of Banks Peninsula (Stewart 2011).

In figure 3.15 the Banks Peninsula data is excluded and only the Central Canterbury Plains data is displayed. This plot shows that the surface water and the groundwater are very similar in their isotopic composition, despite their different overall concentrations, further reinforcing the inference of significant interaction between these waters. Some surface water samples have more positive $\delta^{15}N$ value, between 7.6 and 10‰. These samples could

represent nitrate sourced from cattle manure (Widory et al. 2004; Widory et al. 2005). Alternatively, denitrification could be causing enrichment in both $\delta^{15}N$ and $\delta^{18}O$ in these samples. Denitrification would be further identified by a relationship that showed enrichment in $\delta^{15}N$ with decreasing NO_3^- concentration. The samples from the Central Canterbury Plains suggest that this is not the case (Figure 3.16), as, while there is a loose trend of more positive $\delta^{15}N$ values with decreasing NO_3, the r^2 value of 0.12 indicates that this relationship is not strong. The sampling locations for many of the surface water samples collected on the plains were from small streams near to Lake Ellesmere and bordered by dairy farms, meaning that cattle manure, as a source for the slightly more positive values of $\delta^{15}N$ is not beyond being a possibility.

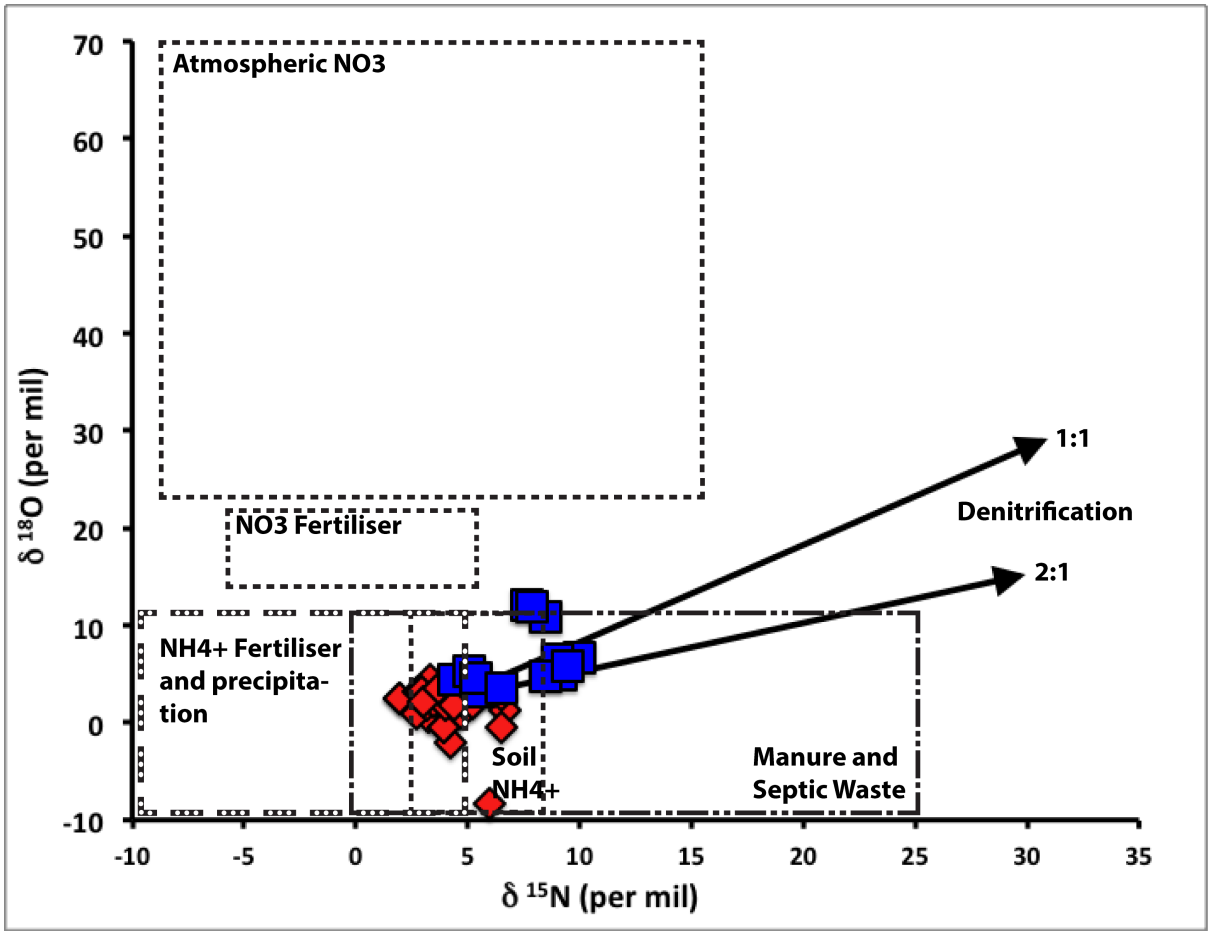

Figure 3.15 $\delta^{15}N$ v $\delta^{18}O$ plot for groundwater and surface water of the Central Canterbury Plains in 2011.

A more thorough discussion on the significance of the isotopic composition of the groundwater samples for the Central Canterbury Plains and their relationships globally, is included in chapter four. Chapter four also focuses on the AMP nitrate plume in an attempt to use stable isotope ratios to demonstrate a clear point source of nitrate pollution in the Ashburton area.

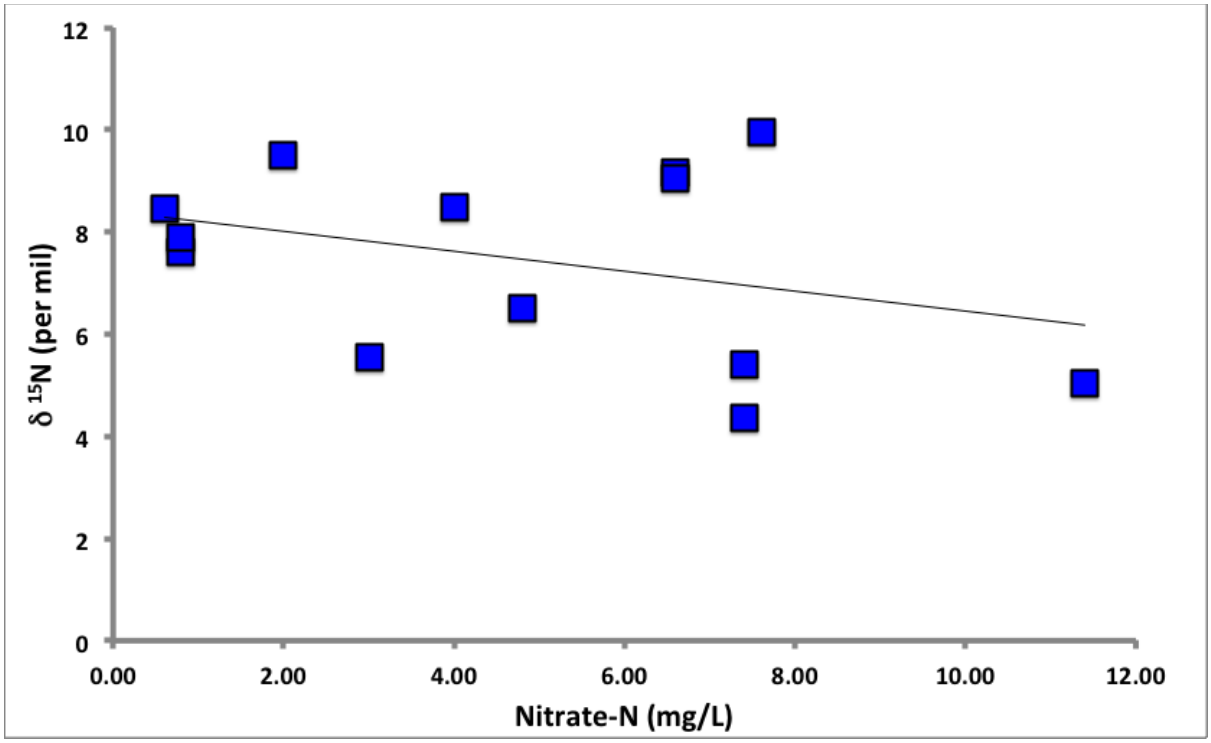

Figure 3.16 $\delta^{15}N$ v Nitrate-nitrogen plot for the groundwater of the Central Canterbury Plains in 2011.

Chapter 4 - Ashburton Meat Processors Nitrate Plume – Geochemistry and Isotopic Signature

4.1. Meat Processing in Ashburton

Ashburton is the service hub for the rural region of Mid Canterbury. As a result, the services in the town are centred on the agricultural sector. This includes meat processing plants for slaughtering stock, the first of which was constructed in Ashburton in the late 1800's (Dynes et al. 2010). At present there are three meat processing plants operating in the wider Ashburton district. These plants apply wastewater to the land via irrigation, which is a source of nitrate contamination in the region.

The study by Hayward and Hansen (2004) focused on three meat-processing plants located in the Ashburton area. They were the Ashburton Meat Processors (AMP) in northeast Ashburton, and Canterbury Meat Processors (CMP) and Silver Fern Farms (formerly PPCS) both in the Fairton-Seafield area approximately five kilometres northeast of the Ashburton township on state highway one. Each of these processing plants has monitoring wells associated with resource consents allowing discharge of water, which must undergo regular monitoring of various geochemical properties, including nitrate concentrations. A number of additional sample wells were also included the Hayward and Hanson survey (2004). The Fairton-Seafield area has several point sources of nitrate. In addition to the disposal sites used by CMP and SFF, there is a third effluent and waste disposal site managed by Talley's Fisheries Ltd, as well as dairy sheds and piggeries. Resource consents for SFF, CMP and Talley's Fisheries to discharge wastewater were granted in 1998, 1999 and 2005 respectively, while any smaller discharges from dairy sheds and piggeries do not require consents. These dictate how the volume and concentration of nitrogen can be discharged onto the land. It is also a requirement for regular sampling to be completed for monitoring. Other consents for

discharge in the area do not require the monitoring that SFF and CMP are required to undertake.

Inland and at a higher hydraulic gradient than the SFF discharge site, concentrations of nitrate-nitrogen are high at 7.4-7.5 mg/L. At the discharge site and down gradient of this discharge site nitrate concentrations are more variable and generally higher. Concentrations decrease with increasing well depth and in deeper wells nitrate concentrations are similar to background levels. Median concentrations onsite were 23, 11.3 and 6 mg/L at depths of 27, 35 and 36 metres respectively. While down gradient the shallower well has a median concentration of 21.7 mg/L, but has reached 33.6 mg/L. Other shallow wells down gradient also have concentrations of nitrate that exceed the MAV, with median concentrations of 20.8, 12.2 and 13.7 mg/L (Hayward & Hanson 2004).

CMP discharges to two sites, a block at Seafield Road and a block at Christys Road. Seafield Road is down gradient from the SFF plant and so even the up gradient monitoring wells show nitrate concentrations above background levels. This site is still adding to the contamination though as onsite wells often recorded nitrate concentrations exceeding 20 mg/L and those down gradient contained levels between 14 and 20 mg/L from 1995 to 2003, higher than the up gradient concentrations. At the Christys Road site even up gradient wells have high concentrations, in the range of 8-12 mg/L, however the reasons for this are unclear. It is suspected to the result of discharge from other, smaller point sources. Onsite concentrations at Christys have been increasing and reached levels of 14-20 mg/L in 2002/2003, while down gradient the shallow wells have exceeded the MAV of nitrate-nitrogen in most samples and show a slight increase over time (Hayward & Hanson 2004). In addition to discharge from CMP and SFF, the 2004 study focused particularly on contamination associated with the Ashburton Meat Processors plant.

4.2. Ashburton Meat Processors - Previous Studies

The AMP plant is located on Bridge Street in Ashburton and has held a Resource Consent for the discharge of water from the plant since 1995. Sampling of the monitoring wells has been carried out since 1992 and the report by Hayward and Hansen analysed the data up to 2003, including a detailed survey in 2000 (Figure 4.1)

Figure 4.1 Nitrate-nitrogen concentrations in the AMP plume in the 2000 survey. Data from Hayward and Hanson , 2004.

The findings of Hayward and Hanson (2004) for the AMP plume are summarised as follows. Up gradient of the plant, the 6 metre deep monitoring well has an average nitrate-nitrogen concentration of 4.2 mg/L. This is comparable to the background average in the area and is below the MAV for nitrate-nitrogen. In contrast the wells located onsite and down gradient of the plant have shown a significant amount of variability in nitrate-nitrogen concentration. Onsite the concentrations in the 9.3 metres deep well have varied from less than 1 to 89 mg/L, perhaps the highest single nitrate concentration ever recorded outside of an evaporate

basin system. This well has a median of 16 mg/L, approximately 5 ppm (50%) higher than the MAV. Farther down gradient nitrate concentrations range from 8.9 to 34 mg/L and the median is slightly higher than the onsite well at 17.6 mg/L. Generally the concentrations of nitrate down gradient are higher than those up gradient, but lower than the onsite concentrations.

There also appear to be other influences on the distribution of nitrate concentrations in the groundwater around the AMP plume. These include, interaction of surface water and groundwater, precipitation, and well depth. Nitrate-nitrogen concentrations nearer the Ashburton River were lower than elsewhere, suggesting that the surface water is recharging the groundwater and diluting the nitrate. A seasonal variation is seen in the nitrate concentrations. This can be correlated with the water level data for the locations and is therefore likely to be related to recharge from either precipitation or irrigation. Concentrations are also lower in deeper wells as the nitrate plume has not reached this depth, at least not yet (Hayward & Hanson 2004).

In 1995 AMP Limited was granted a consent to discharge waste to land (Environment Canterbury 1995), this was reviewed and many changes made to management practices in 2003 when rising nitrate concentrations became a major concern (Keast 2004). Changes to waste discharge practices included replacing old irrigators, re-sowing all pasture within the disposal area and the implementation of the "cut and carry" technique. This process involves cutting and removing pasture on which wastewater is sprayed and using it as feed offsite. This means that nitrate absorbed by the grass is not recycled into the same system. Pig hair and paunch is also applied to a company worm farm that converts the waste to vermicast, which is then removed and taken to a landfill.

4.3. Environment Canterbury Data

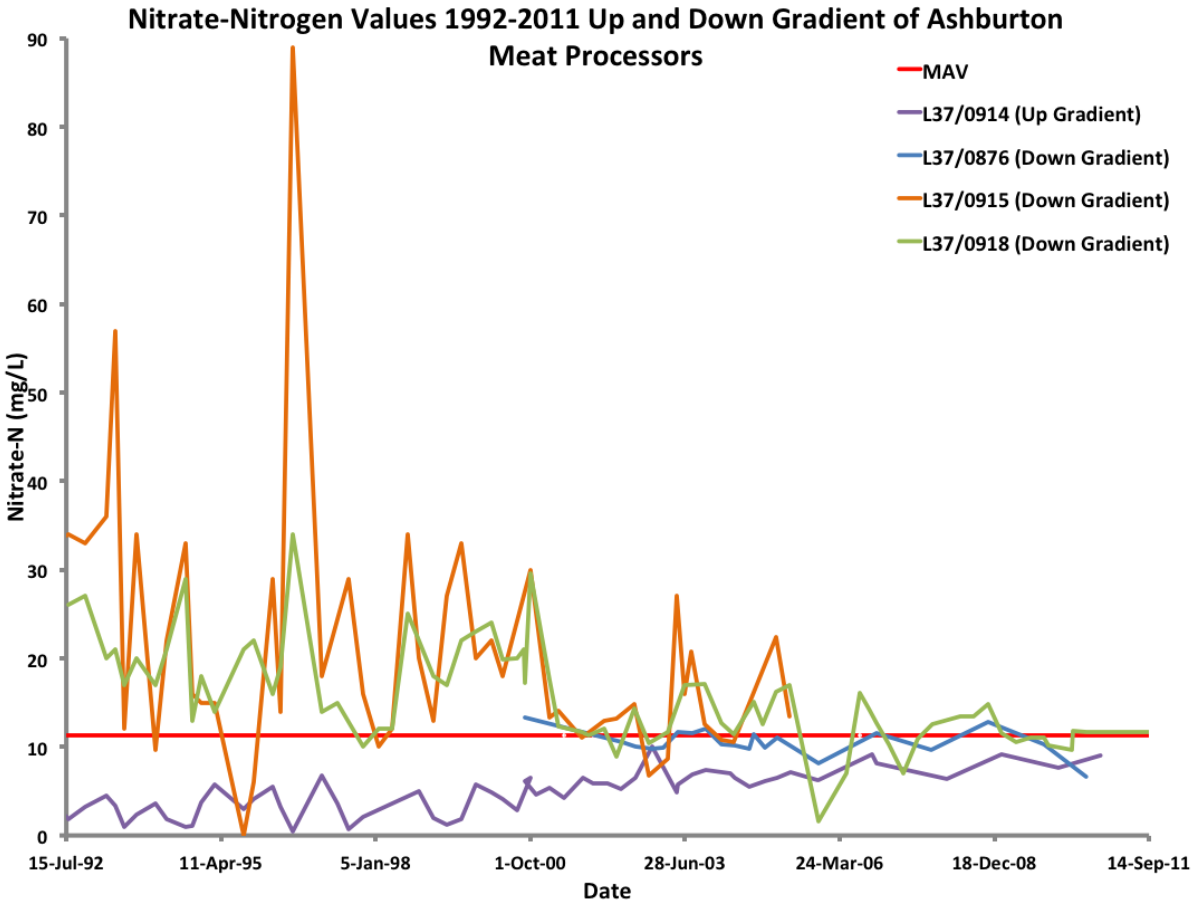

Figure 4.2 Nitrate-nitrogen concentrations for wells up gradient and down gradient of the AMP plant, showing trends between 1992 and 2011.

Environment Canterbury has sampled groundwater around the AMP plant regularly since 1983. At some locations samples are taken quarterly, while other wells are on an annual assessment program. These data, coupled with more in depth studies such as the one outlined above by Hayward and Hansen, make it possible to identify both spatial and temporal trends in the nitrate concentrations. The temporal trend for nitrate concentrations both up and down gradient of the AMP plant (Figure 4.2) was examined and showed very high nitrate concentrations being reached in 1996. Since then there has been a gradual decline in concentrations down gradient of the plant, with a significant drop and subsequent stabilising of values in the early 2000's. Meanwhile nitrate concentrations in the up gradient monitoring well, L37/0914, has shown a gradual increase and now has nitrate concentrations almost

indistinguishable from down gradient sample points. This suggests that the management practices discussed above are now having a positive effect on the groundwater quality, while the data also highlights wider concerns regarding the rising nitrate concentration in groundwater throughout the plains.

4.4. 2011 Sampling

Sampling associated with this thesis was undertaken in November 2011 to obtain a snapshot of the current situation around the AMP plant and compare this with historical data held by Environment Canterbury. Eight water samples were collected, including two groundwater samples up gradient of the plant, at different depths, one sample location on an approximately equal groundwater flow contour to AMP, and three at varying distances down gradient of the plant (see Appendix three for sample site details). Two surface water samples were alos obtained, for comparison purposes from a stagnant pond in a business park development in Ashburton and from a small stream that flows through the Ashburton Domain (Figure 4.3).

At groundwater sample sites, bores were purged so as to remove any stored water. The volume of water pumped was determined by the equation:

$$(\text{Water Depth} - \text{Screen Depth}) \quad \text{x} \quad \pi(\text{Well Radius})^2$$

Samples were then taken in either a 10 or 20 L container as well two 50 mL samples and a fourth sample for dissolved inorganic carbon in a helium filled extainer. Temperature, conductivity and pH were also measured in the field. Samples were filled to the very top of all containers and sealed. Additionally, in field titrations were completed using 50 mL water samples and incremental additions of 0.01 N H_2SO_4 in order to determine HCO_3^- alkalinity.

After the fieldwork component, the DIC samples were analysed for $\delta^{13}C$- DIC, within 24 hours at the Universtiy of Canterbury Stable Isotope Laboratory. For anion concentration

determination, 10 mL of sample was filtered using a 0.45 micron filter fitted to a 25 mL plastic syringe and these samples were then analysed in the University of Canterbury's RF-IC. All of the major anions in the samples were determined using this process. A further 50 mL sample was also filtered and sent to the United States Geological Survey in order to determine $\delta^{18}O$ and $\delta^{15}N$ values. This was completed using the bacterial denitrifier method (Sigman et al. 2001; Casciotti et al. 2002; McIlvin & Casciotti 2011) as outlined in chapter two.

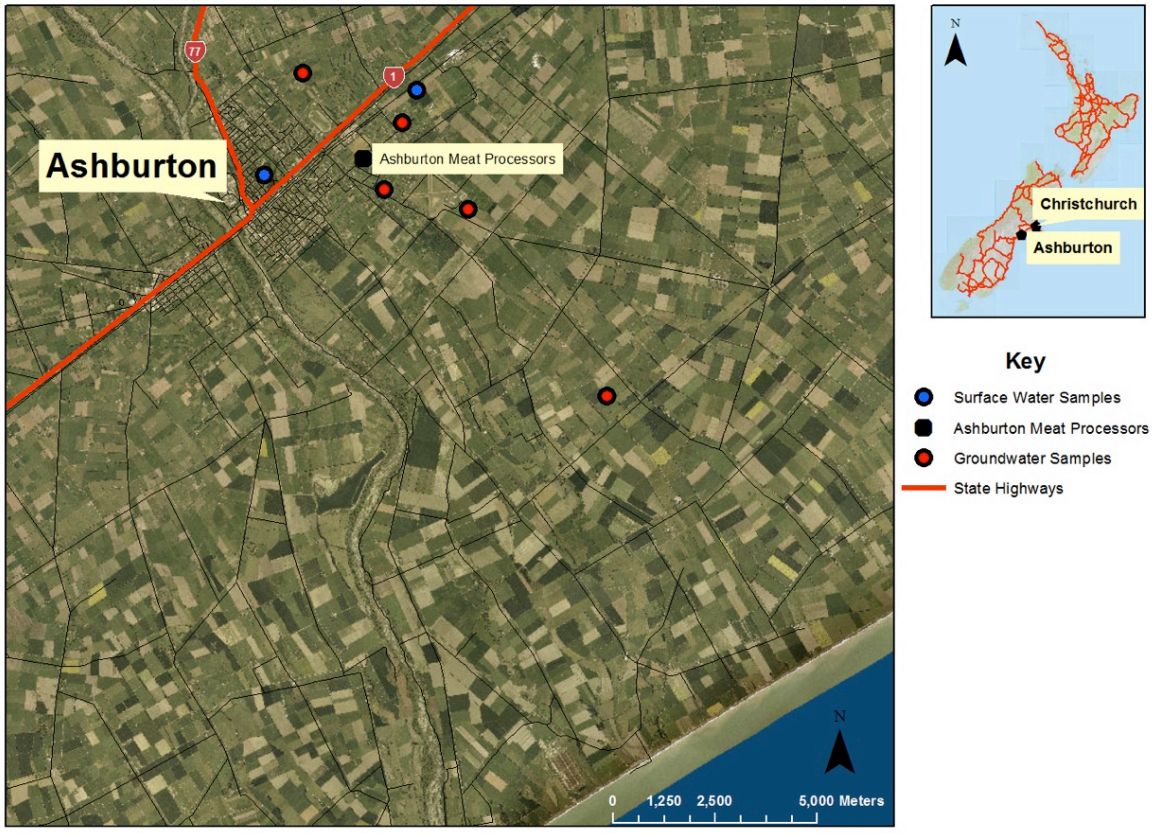

Figure 4.3 Sample locations for November 2011 sampling around the AMP plant in Ashburton.

4.5. Ashburton Meat Processors Nitrate

In this study, at all of the sites sampled, the nitrate-nitrogen concentration observed was below the MAV of 11.3 mg/L (Table 4.1). Three samples recorded values that exceeded half of the MAV. All three of these samples were located down gradient of the AMP plant. The two groundwater samples taken up gradient, and one taken on a similar groundwater gradient

to the plant were slightly below half of the MAV, but still above what would be considered a natural background concentration for the region (Figure 4.4). The concentrations do not suggest that the nitrate is directly related to waste being discharged from the AMP plant as similar concentrations occur throughout the plains (chapter three). The two surface water samples both had relatively low (0.73-1.31 mg/L) nitrate concentrations.

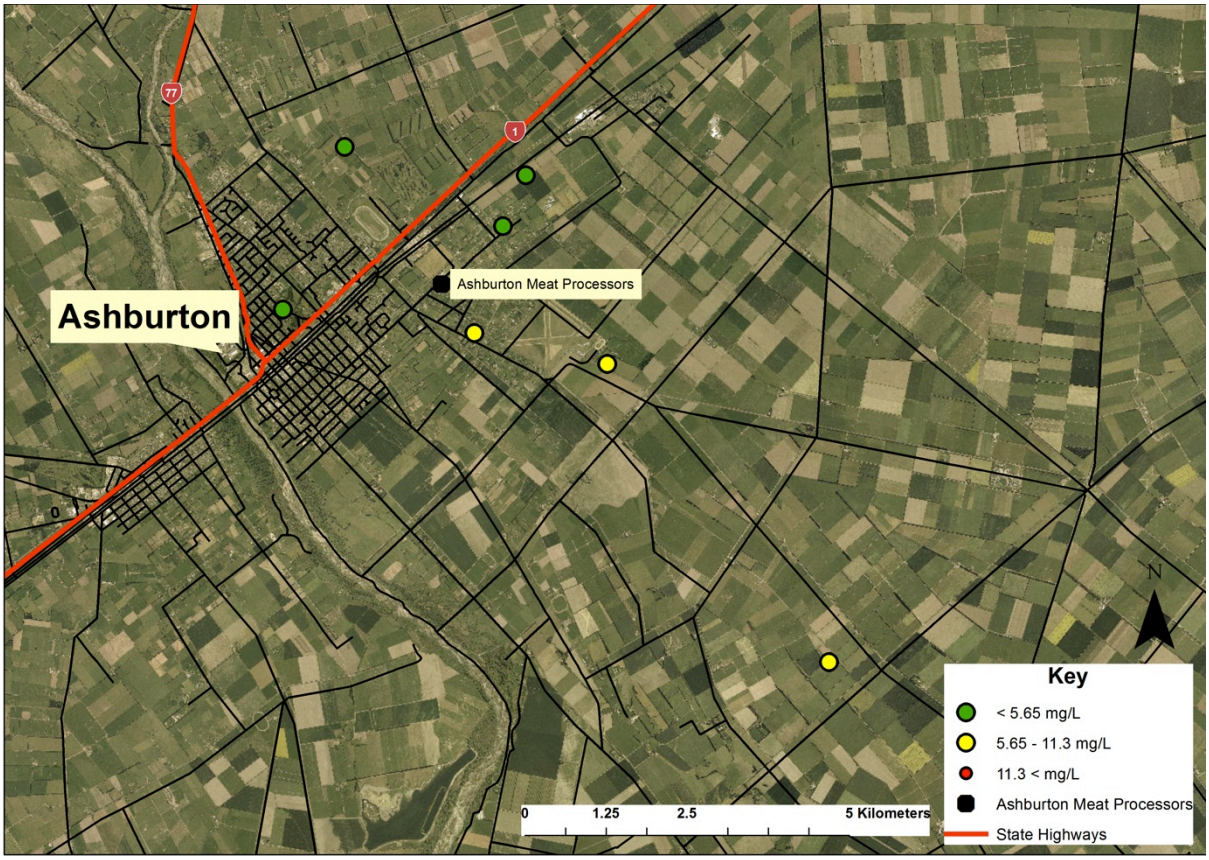

Figure 4.4 Nitrate-nitrogen concentrations of the AMP plume during the 2011 sampling.

While all of the concentrations recorded down gradient are higher than the median of the samples collected across the Central Canterbury Plains in 2011 (6.98 mg/L) they fall within one standard deviation of this data (Figure 4.5a). This can be compared with the data from Environment Canterbury around AMP in 2000 (Figure 4.5b), when nitrate concentrations were also higher than the median for the whole of the Canterbury region. In 2000 there are also a significant number of nitrate concentrations that are higher than the standard deviation for the data in that year. This indicates that in 2000 there was a notable nitrate source in the

area, this was presumed to be the AMP. A trend of gradually declining nitrate concentrations away from AMP is also present providing further evidence for an association with the disposal of waste at this site. The 2011 data do not show the same trend of higher nitrate concentrations, as in the year 2000 down gradient of the AMP and the nitrate concentrations are more consistent along the entire transect.

Using hydraulic conductivity and the hydraulic gradient it is possible to approximate the rate at which groundwater is flowing through the subsurface in the Ashburton area. This would also indicate the rate at which any contaminant such as nitrate is moving through the groundwater and the length of time it would take to be removed from the system, assuming uniform input of the contaminant and uniform consistent flow. In the Ashburton area the hydraulic conductivity is estimated to be between 500 and 630 m/day (Bal 1996). The heterogeneity of the aquifers leads to substantial variation (100 to 1585 m/day) in hydraulic conductivity across the Canterbury Plains (Bal 1996), even in the relatively short distance between the Ashburton township and the coast. However, hydraulic conductivity values used here are consistent with the literature for similar geological settings of gravels and coarse sands, where values can range from 250 m/day to 25 000 m/day (Dielman 2005). Thus, the following results are a rough approximation of the travel times. Using these values the flow velocity was calculated and subsequently the length of time required for groundwater to travel from AMP to the coast. This value ranged between 14.6 and 18.4 years, depending on the conductivity value used (see Appendix 4).

The decrease in nitrate concentrations down gradient of the AMP plant over the last ten years, accompanied with the documented amendments to the disposal practices of AMP and the flow velocity of the groundwater beneath Ashburton, suggests that the significant plume of nitrate recorded as being sourced from AMP during the 1990's and early 2000's has now passed, or is in the final stages of passing through the system.

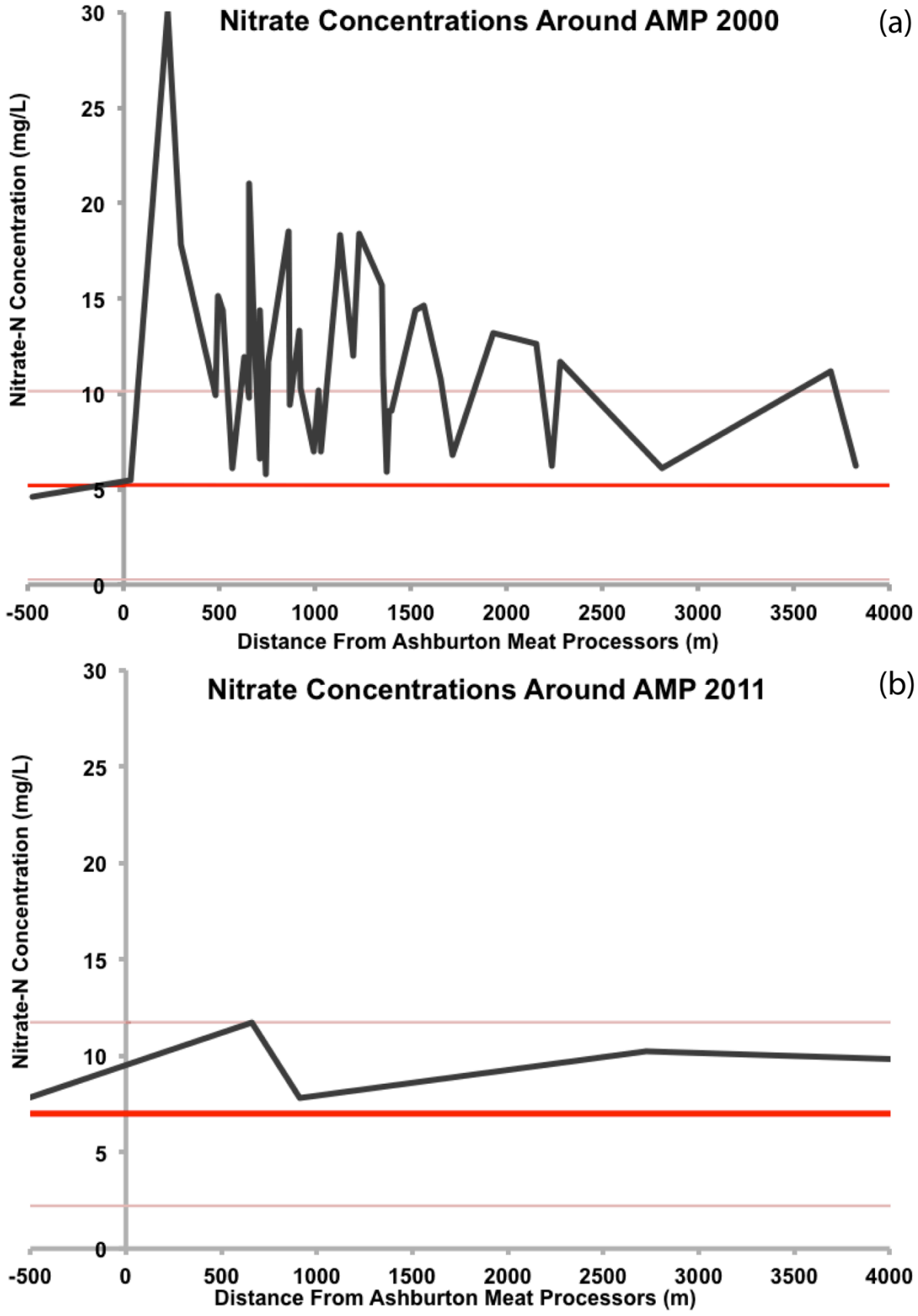

Figure 4.5 Nitrate-nitrogen concentrations along a transect across the AMP plant in 2000 (a) and 2011 (b). Data for 2000 is sourced from Environment Canterbury wells database.

Well Number	Nitrate-N mg/L	Fluoride mg/L	Chloride mg/L	Bromide mg/L	Nitrite mg/L	Sulfate mg/L
L37/0786	4.79	0.07	3.64	N/A	0.01	8.42
L37/0786-2	3.76	0.04	2.90	<0.01	0.01	8.88
L37/1013	5.51	0.10	4.23	N/A	0.02	7.80
L37/0964	7.84	0.07	6.08	N/A	0.02	11.07
L37/1195	10.25	0.07	9.23	N/A	N/A	13.14
L37/0158	8.47	0.08	7.29	N/A	N/A	11.54
Business Park Pond	1.31	0.02	3.87	N/A	N/A	1.48
Ashburton Domain Stream	0.73	0.04	1.74	N/A	0.00	2.38

Table 4.1 Anion data for samples collected around the AMP plant is Ashburton during November 2011.

4.6. Other Anion Data for the Ashburton Area

4.6.1. Nitrite

Measurable nitrite was found in four of the six groundwater samples collected in the Ashburton area. Two of the samples were from locations up gradient of the AMP plant, one was at a similar groundwater contour and the last was immediately down gradient of the plant. This suggests that the AMP itself has little influence on contributing nitrite to the groundwater pt oresent. The highest nitrite value recorded was 0.0220 mg/L, below the long term provisional maximum allowable value of 0.2 mg/L and well below the short term MAV of 3 mg/L (Ministry of Health 2008).

4.6.2. Chloride

Chloride data for the AMP transect is similar to the pattern for the nitrate. All of the samples have chloride concentrations below 10 mg/L, which is not unusual for the Canterbury Plains, where the median chloride concentration is 11 mg/L and the standard deviation is high, at 268 mg/L. This is in contrast to the medians shown in figure 3.10 around the AMP, where values are often above 10 mg/L. There is close correlation between the chloride concentration and the nitrate concentration as shown by the trend line. This suggests the source is the same for both chloride and nitrate. These concentrations further suggest that the pollution from

waste associated with the AMP has reduced and now does not appear to be significantly different from background values.

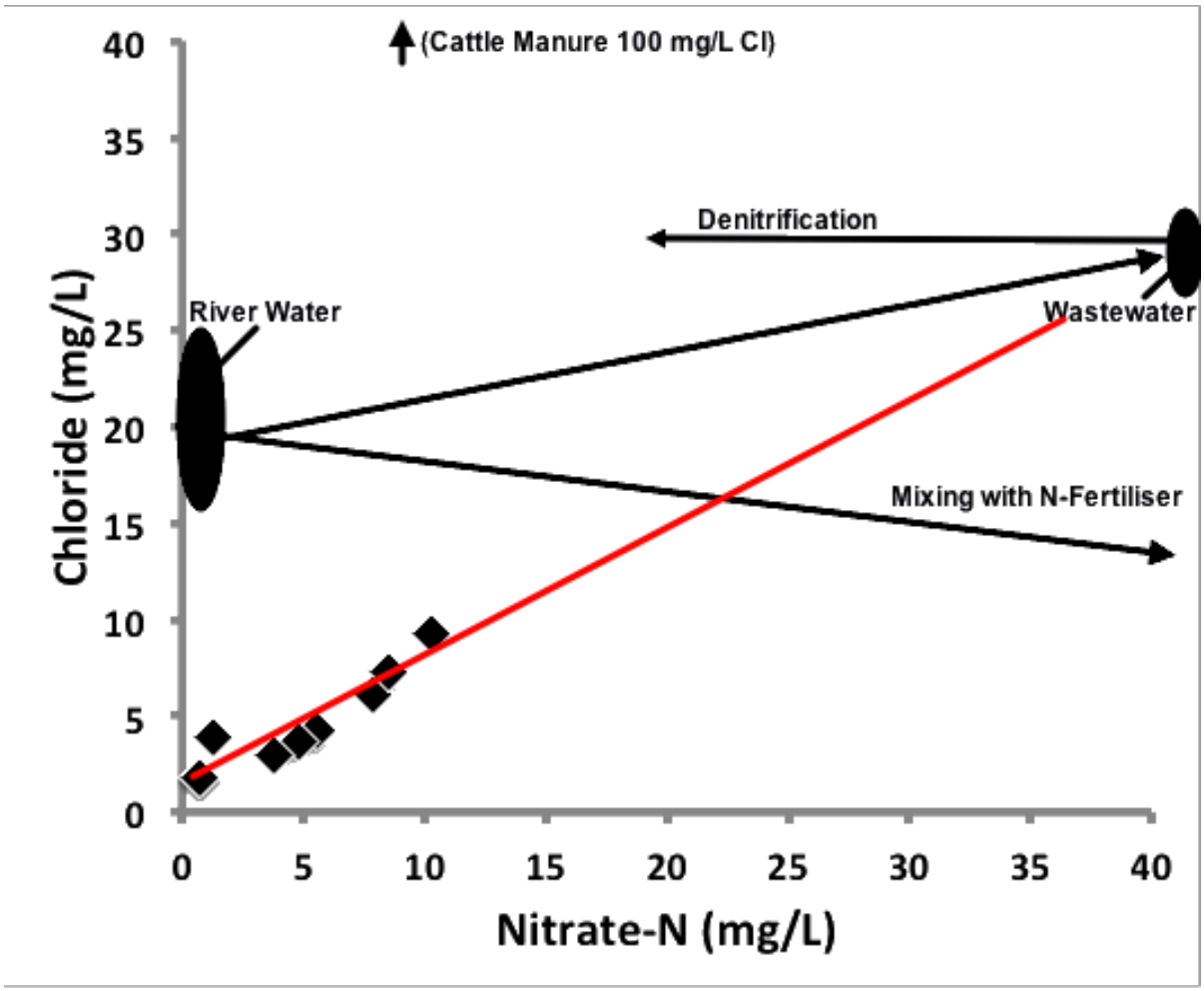

Figure 4.6 Chloride concentration v nitrate-nitrogen concentration for the transect across the AMP plant with expected concentrations of end members from Widory et al. 2005. The red line is a trend line and has an r^2 value of 0.87.

Chloride can be plotted against nitrate concentration and used to further assist with the identification of contamination to water. Figure 4.6 shows an increasing chloride concentration as nitrate concentrations increase. However, the chloride concentrations in the figure are too low to be connected with a specific source and would suggest that natural nitrate is the source of any elevated nitrate. This is consistent with studies that have used this type of bivariate analysis in other locations (Williams 1998; Widory et al. 2005; Koh et al. 2010). High (100 mg/L) chloride concentrations with moderate (2-12 mg/L) nitrate-nitrogen

concentrations indicate cattle manure source, while very high (100 mg/L<) nitrate-nitrogen concentrations and low (<10 mg/L) chloride concentrations are typical of nitrogen fertilisers.

4.6.3. Sulphate

Sulphate is used in many different industrial activities including production of fertilisers, insecticides, chemicals, and fungicides, amongst others. Similar to chloride, sulphate does not have detrimental effects on human health or the ecosystem, unless present at extremely high levels (>600 mg/L), where effects are minimal. In drinking water, sulphate may become noticeable to taste if concentrations are above 250 mg/L, while if the concentration is above 600 mg/L, it may have a laxative effect. Sulphate in groundwater will naturally range in concentration from 0 to 250 mg/L, with most samples being below 10 mg/L (World Health Organisation 2004).

Table 4.1 reports sulphate data original to this thesis, and that ranges from 1.5 mg/L to 13.1 mg/l for both surface water and groundwater. These levels do not suggest any significant source that could cause increased sulphate and can be considered unremarkable.

4.6.4. Bicarbonate (Alkalinity)

Bicarbonate concentration is measured as the alkalinity. This is because in neutral conditions for groundwater in Canterbury, bicarbonate is the dominant ion that contributes to alkalinity. The assumption is therefore made that alkalinity represents bicarbonate concentration (Hanson & Abraham 2009). Figure 4.7 shows the $\delta^{13}C$ of the dissolved inorganic carbon [DIC] in the water samples taken against the inverse of the DIC concentration, assumed to be equivalent to HCO_3^- alkalinity. This separates the results into three distinct categories. All of the groundwater samples are grouped with more negative $\delta^{13}C$ and lower alkalinity values while the business park surface pond has a more positive $\delta^{13}C$ value and a higher alkalinity concentration. The stream in Ashburton Domain plots between the two.

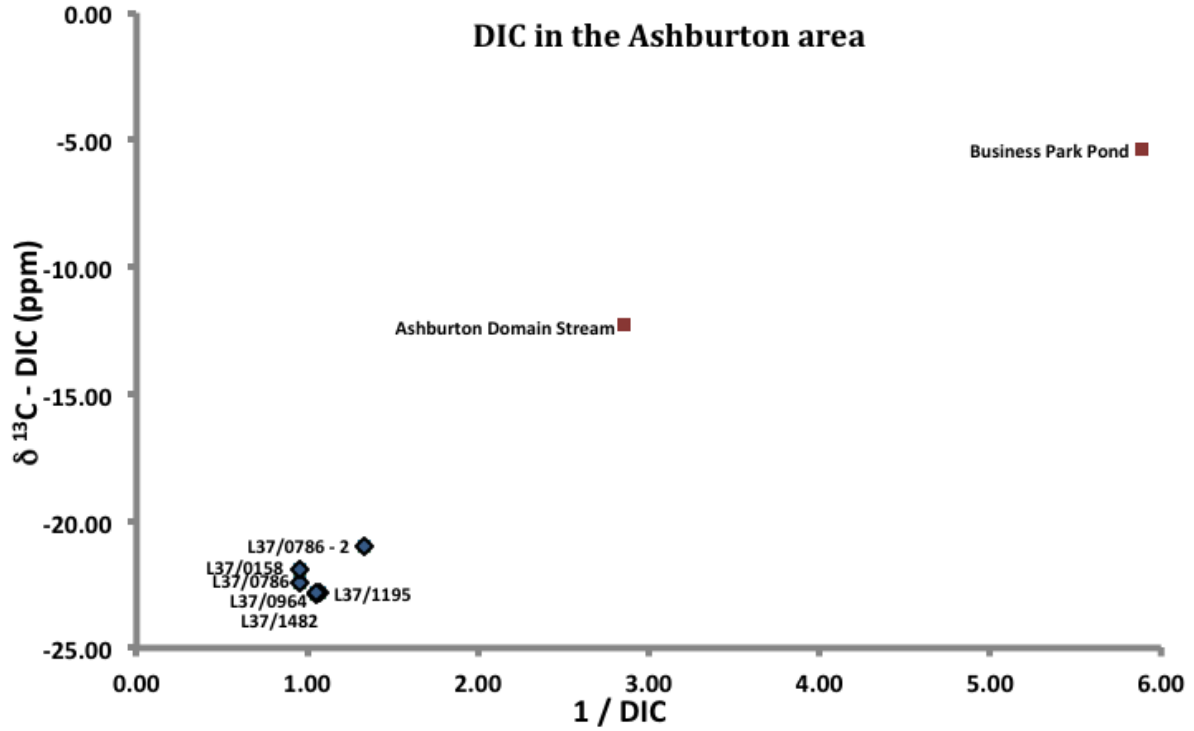

Figure 4.7 $\delta^{13}C$ of DIC v alkalinity plot for the AMP transect.

The data (see Appendix five) for the groundwater samples and the stream in Ashburton Domain, are consistent with previous studies completed on the Canterbury Plains (Taylor & Fox 1996; Stewart 2012). Surface water will generally contain a low amount of DIC due to the equilibration of atmospheric CO_2 and will have a $\delta^{13}C_{DIC}$ value also similar to that of atmospheric carbon dioxide (-8‰) (Wang et al. 1998). This pattern has been previously observed in the Waimakariri River which has $\delta^{13}C$ of -7‰ and relatively low DIC concentration (Stewart 2012). Groundwater will have variable amounts DIC and $\delta^{13}C$ values, as there is a significant influence from the soil and the local bedrock that the water is flowing through. In Canterbury the geology has very little influence on the carbon isotopes as the glacial and fluvial greywacke sediment present is silicate rich and carbonate poor. Therefore it is the oxidation of organic material that will serve as the primary control on groundwater DIC carbon isotope compositions. Biogenic derived DIC can be very high with very low $\delta^{13}C$ values of ~-25‰, similar to the values observed in groundwater in Canterbury (Stewart 2012). The Ashburton Domain stream has a $\delta^{13}C$ value of -12.25, more negative than that

observed in the larger, alpine fed rivers such as the Waimakariri. This is indicative of a stream that sources at least some of the water from groundwater, or from a biogenic carbon source that could include particulate organic matter. The groundwater samples plot in a similar range as has been observed elsewhere on the Canterbury Plains. The business park pond sample had a very low DIC and much less negative $\delta^{13}C$ value than even most surface water samples. This is likely to be a result of the pond being stagnant water whereby evaporation enrichment may have changed both DIC and $\delta^{13}C$-DIC. As the water is constantly open to the atmosphere the DIC is able to undergo exchange with atmospheric CO_2, therefore pushing the water DIC towards a $\delta^{13}C$ of -2 to 0‰ (7‰ more positive than atmospheric CO_2 due to equilibrium fractionation.

4.7. Nitrate Isotopes of Water in the Ashburton Area

The $\delta^{15}N$ values of nitrate in groundwater in the Ashburton area are all between +3.05 and +6.47, while the $\delta^{18}O$ of the nitrate values are between -0.39 and +3.49. This data for nitrate in the groundwater around the AMP shows no obvious signature that unequivocally links it to an anthropogenic source. The $\delta^{18}O$ v $\delta^{15}N$ data plotted in figure 4.8 suggests the nitrate is similar to 'normal' soil nitrate (Kendall et al. 2007), and is intrinsically indistinct from the rest of the Central Canterbury Plains (Figure 3.13). This suggests that either the wastewater that has caused elevated nitrate down gradient of the AMP plant is either isotopically the same as the sources contributing to water elsewhere on the plains, or is further evidence to suggest that the nitrate plume associated with the plant in the past has now all but entirely moved through the area, or both. All lines of evidence support the single interpretation that nitrate in the Ashburton area is now derived from the same diffuse sources that affect the rest of the Canterbury Plains.

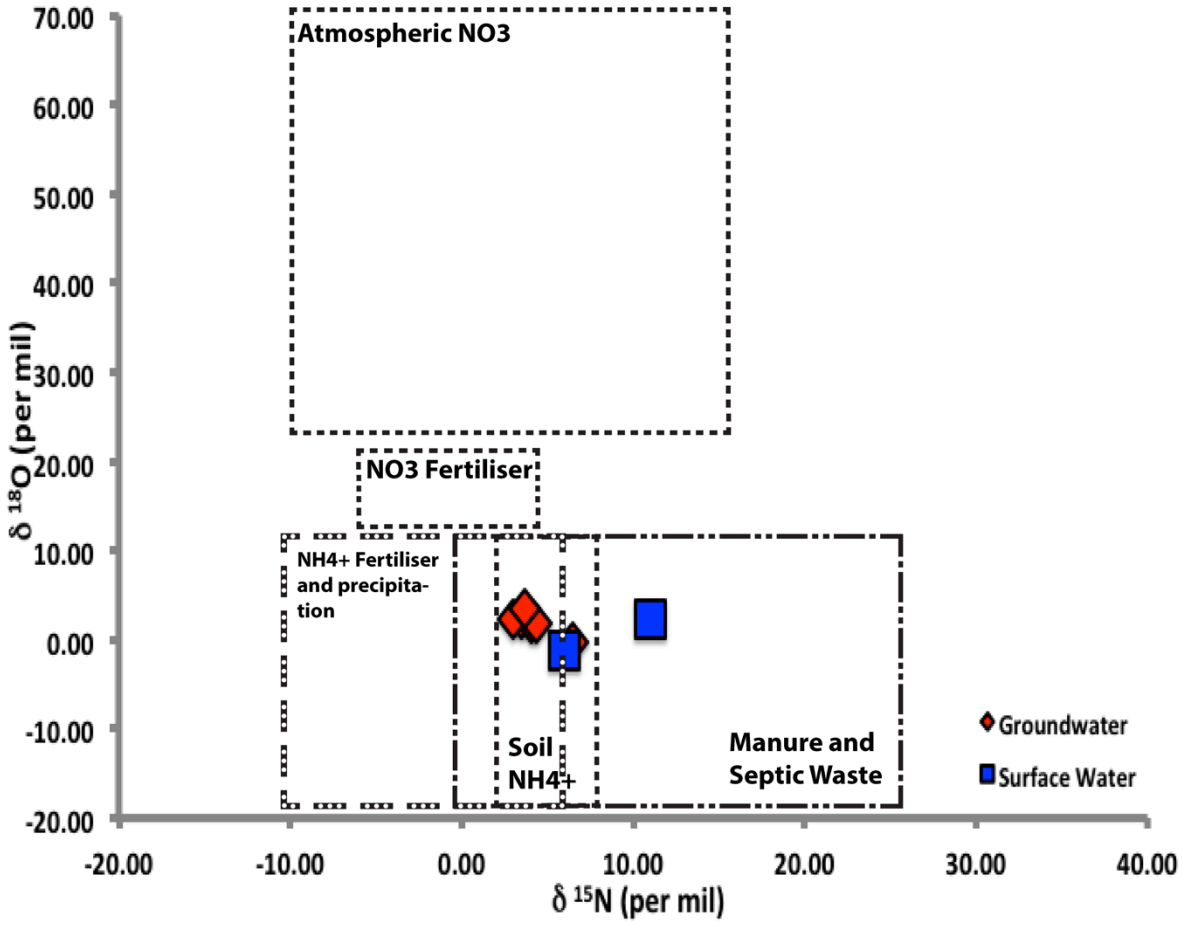

Figure 4.8 Plot of $\delta^{18}O$ v $\delta^{15}N$ of nitrate for the AMP transect, showing both groundwater and surface water.

The lack of variation seen in the isotopic composition of nitrate across the Central Canterbury Plains is an important new discovery, original to this thesis, as it strongly suggests that the use of a dual isotope approach for source identification of nitrate pollution will not provide forensic 'proof of source' in Canterbury systems, unlike elsewhere on the planet. An explanation for this novel discovery requires further research, though some preliminary theories will be explored briefly in this discussion. These include: 1) a single dominant source of nitrate, namely clover, is responsible for the isotopic signature; 2) the effects that irrigation has on natural nitrate sources, by mobilising nitrate previously locked in the soil; 3) the processes that nitrate is subject to as it is leached through the soil column, such as nitrate immobilisation, and; 4) the role that plants and microbes have in altering the isotopic signature of nitrate, through uptake of nitrate before recycling it back to the soil.

4.7.1. Nitrate Immobilisation in Soil

Soil studies suggest that nitrate can be immobilised by microbial incorporation, causing a conversion to organic nitrogen (Mengis et al. 2001; Panno et al. 2006). Immobilisation has been particularly evident following the addition of inorganic fertiliser to the land. Subsequently, the isotopic composition of nitrate that eventually reaches the groundwater is altered and will likely appear to be similar to soil derived nitrate that has undergone the same process. An internal cycling of nitrogen, known as the mineralisation-immobilisation turnover (MIT) results in the immobilisation of nitrate as organic nitrogen, followed by remineralisation to ammonium and nitrification back to nitrate (Mengis et al. 2001). The nitrate is then returned to the soil and eventually leached to the groundwater with a $\delta^{18}O$ value that is different to the nitrate initially applied (Panno et al. 2006) and possibly some enrichment in ^{15}N (Mengis et al. 2001). Subsequently the isotopic signature, especially of $\delta^{18}O_{NO3}$ will not be dissimilar to that of natural nitrate with a soil source. In order for this process to occur the residence time of the nitrate originally applied as fertiliser in the soil must be relatively high (Mengis et al. 2001). This theory helps explain the lack of a nitrogen fertiliser isotopic signature in the Canterbury groundwater, when it is known that there is application of such fertilisers across the region. However, this theory, to be true, requires that the residence time of nitrate is much longer that the residence time for water in the near surface environment.

Soils in the Canterbury region are largely brown, pallic and gley soils, with stony brown soil accounting for a majority of the land on the Canterbury Plains. These soils have a low water holding capacity, between 90 and 150 mm (Morgan et al. 2002) and when water is applied, either through rainfall or irrigation in excess of the holding capacity, it will flow to groundwater or into surface waterways via overland flow (Moot et al. 2010). As a consequence, this water will transport any excess nutrients with it. In other words, the high

naturally high soil nitrate content in the Canterbury region could be mobilised by excessive pulses of water application. Therefore the application of fertiliser must be carried out with consideration for the amount of water in, or being added, to the soil, by either irrigation or precipitation. The ability of the pasture to take up the applied nutrients must also be factored in.

With the increase in fertiliser use and change in the pasture cover of the land, soils in Canterbury are able to withstand more nutrient input. This is due to the increased biomass taking up the added nitrogen (Woodfield & Caradus 1996; Tillman 1998). But the nitrogen must go somewhere and this in turn increases the potential for nitrate to be leached to the groundwater. The isotopic signature will link the nitrate to a natural soil source as a result of the immobilisation of the fertiliser nitrate in the soil, which converts fertiliser inputs to nitrogen and subsequently overprints the isotopic signature to that of microbiologically derived soil nitrate. This means that a fertiliser source of nitrate and a natural soil source of nitrate will only be distinguishable when the fertiliser is leached straight to the groundwater with little interaction with the soil or the pasture.

4.7.2. Natural Soil Nitrate

Prior to humans arriving in New Zealand, the Canterbury Plains were heavily forested by podocarp and hardwood forest (McGlone 1989). Deforestation began with the arrival of Polynesian people to New Zealand, approximately 1000 years ago, who cleared some of the forest, and converted the land cover to tussock and shrub land. Further deforestation by burning continued with the arrival of Europeans, who further converted the land to pastures suitable for cropping and agriculture (McGlone 1989; Ogden et al. 1998).

Different land cover will lead to different concentrations of nitrate in the soil and in turn the amount of nitrate that is available for leaching to groundwater systems (Scanlon et al. 2005).

Nitrate concentrations of soil in forested areas are generally lower than that of similar soils in a grassland area. This is due to the internal cycling of nitrogen that occurs in a forest, with a significant amount of uptake into trees and shrubs. It would therefore be expected that a change in land cover on the same soils would affect the nitrate concentration of the soils and subsequently the amount of nitrate being leached to groundwater. Nitrate is constantly removed from the soil system by the biomass (Sloan et al. 1994). Thus, the removal of a significant amount of biomass leads to less nitrate being removed from the soil by plants. There are some cases where decreases in soil nitrogen following deforestation has occurred (Neill et al. 2001), though the pasture cover that replaced these forests was purely a grass based system without the clover as used throughout Canterbury. In this example, there is no additional nitrate fixation after the forest is cleared. Once the nitrogen stored in the biomass is removed from the system, the soil must be supplemented in order to promote any grass growth.

Quite obviously, a change in land cover through deforestation has occurred on Canterbury Plains over the past four hundred years. This wholesale change in land use provides a plausible explanation for the similarity in nitrate isotope values observed in Canterbury and other New Zealand groundwater locations such as Manakau in the Horowhenua (McLarin et al. 1999). Further investigations focusing on residence and travel time of water and nitrate would be required to test this hypothesis, including the sampling of groundwater beneath any remaining pockets of native forest to obtain nitrate concentrations as well as the isotopic signature of the nitrate. Age dating of water along transects parallel to the hydraulic gradient would assist with matching changes in nitrate concentrations in the groundwater and periods of significant forest cover removal by both Polynesian and European settlers in New Zealand. Additionally, soil sampling to investigate the nitrate concentrations and isotopic signatures in

different soil types, would also provide further information as to the source and fate of nitrate.

4.7.3. Irrigation

High water input to soil can mobilise naturally occurring nitrate that is locked in the soil. This is seen at a site in Hanford, Washington where there is nitrate contamination from wastewater. However, not all of the nitrate in the groundwater at this site is attributable to wastewater sources. The reason provided for this is that the shear volume of wastewater deposited onto the land, mobilise natural reservoirs of nitrate in the soil. Therefore, the nitrate in the groundwater is sourced from both the wastewater itself, and mobilised nitrate previously stored in the vadose zone (Singleton et al. 2005). A similar scenario could exist for the Canterbury Plains and would be related to the deforestation mentioned above. The biomass removal results in increased soil nitrate that can then be mobilised by the irrigation water.

Irrigation in Canterbury first occurred at a substantial scale in 1944 when the Rangitata Diversion Race was brought into operation. This provides 64,000 ha of land with water drawn from the Rangitata River (Pangborn & Woodford 2011). Since then several community schemes as well as groundwater sources have been used to irrigate land in Canterbury for a variety of land uses. Over 400,000 ha of land is now thought to be irrigated in Canterbury (Pangborn & Woodford 2011), equivalent to just under one quarter of the total area of the Canterbury Plains. This additional water may bring the soil to its maximum water holding capacity, at least ephemerally. Therefore, adding further water, either through excessive irrigation or unexpected rainfall, can potentially result in soil nitrate leaching to groundwater. Nitrate held in the soil is mobilised by the additional flow due to higher water application, and travels to the groundwater and surface water.

4.7.4. Clover

The main pasture type used for farming, particularly dairy farming in the Canterbury region is a clover and ryegrass mix (de Klein et al. 2010). Accurate measurements of the total land covered by clover or other grasses are difficult to ascertain, and such surveys have not been carried out to my knowledge. However, it is highly likely that clover has been a significant part of pasture since early Europeans undertook clearing of forest and shrubs. Clover is a nitrogen fixing plant and will contribute nitrogen to the soil and potentially underlying aquifers as a consequence.

Recent investigations into whether nitrogen fixing clover, inorganic fertiliser, or a combination of the two will provide more productive land for agriculture have been undertaken (Harris et al. 1995; Woodfield & Caradus 1996; Tillman 1998). Though increased production does not necessarily lead to higher profits due to the cost associated with fertiliser application. Therefore, pay-outs for milk solids and the cost of fertiliser are also considerations for farmers and are factors that will contribute to the nitrogen input of the two sources of nitrate. Little consideration has been given to whether water contamination is different depending on if the source is clover or nitrate fertiliser, or a combination of the two.

The oxygen and nitrogen isotopic composition of nitrate originating from clover will be in the natural soil range, this is the same composition that is observed in all groundwater and most surface water samples throughout Canterbury. The combined factors of the ubiquitous presence of clover in dairy farm pastures of in New Zealand, and the isotopic compositions seen in both Canterbury and the Horowhenua (McLarin et al. 1999), lead to the hypothesis that much, if not all, of the nitrate contaminating New Zealand's water bodies is sourced from nitrogen fixed by clover. However, continued monitoring and research into the contribution from clover is required as there remains an on going change towards higher fertilisation rates

on dairy farms (Statistics New Zealand 2006). Temporal aspects must also be investigated in course.

4.8. Nitrate Isotopes in a Global Context

Globally, nitrogen and oxygen isotopes of nitrate have proven to be useful for identifying different sources of pollution to groundwater and surface water (Kendall et al. 2007; Xue et al. 2009). However the results presented here show that in the Canterbury environment this forensic tool may be limited. The sources contaminating the groundwater in Canterbury with nitrate appear to be similar to other locations worldwide, though as suggested above, maybe affected by different processes including, MIT, clover, mobilisation by irrigation and deforestation.

In chapter three a comparison was drawn with the agricultural areas of California in the United States and the similar patterns of nitrate contamination over a comparable scale (Figure 3.12). It is however, highly likely that the nitrate, while appearing in comparable concentrations, is originating from different sources than in California. Nitrate stable isotopes and farm management practices form the basis for this interpretation.

Stable isotopes of nitrate in California groundwater show a range of different sources of nitrate contamination to the water systems. A significant portion of the high nitrate concentrations are from mixed sewer and manure sources, along with some contribution from both inorganic fertiliser and soil nitrate locally (Williams 1998; Pellerin et al. 2009). However, most of the nitrate is considered to originate from cropland (Harter & Lund 2012). Analysing the inputs to cropland, synthetic fertiliser and dairy manure are shown to be the major contributors of nitrate to groundwater in the horticultural areas and therefore determine the nitrate isotope compositions seen in the region. In order to understand the reasons why

nitrate sources are isotopically distinct in California, but not in Canterbury, the farming practices used in both regions must first be examined.

As established in chapter one, Canterbury dairy farms maintain some of the highest cattle stocking rates in New Zealand at 3.28 cows per hectare. Comparatively, dairy farms in California have a stocking rate of 20.9 cows per hectare (van der Schans et al. 2009). Animals are housed in freestall areas that have exercise yards comprised of compacted bare soils. Freestalls contain concrete flush lanes for the removal of solid and liquid manure. Manure is then separated and the liquid is stored in soil lined holding ponds while the solid waste is stacked on concrete. The solid waste is then reused for freestall bedding, soil amendment, or off-farm applications, while the liquid waste is used to fertilise fields through fertigation. In the past, the undiluted liquid waste was applied to fields directly (Meyer et al. 1997; van der Schans et al. 2009). These farming practices concentrate nitrate sources into small areas, and especially in the case of liquid waste, provide a significant source of nitrate to the groundwater. The storage of the liquid waste in ponds promotes the conversion of ammonium to ammonia through ammonia volatilisation (Lockyer & Whitehead 1990). Volatilisation of the ammonia will lead to the enrichment of residual ammonium in ^{15}N and produce nitrate $\delta^{15}N$ values that are much more positive. Once nitrified, approximately 8.1 and 13.9 ‰ (Aravena et al. 1993), falling in the category for manure on a $\delta^{18}O$ v $\delta^{15}N$ plot. Ammonia volatilisation will occur to a lesser extent in Canterbury due to the urine being deposited immediately onto the pasture and not being stored for a prolonged period in a pond. This could explain why $\delta^{15}N$ values in Canterbury are not as positive as in California. In short, there is likely less enrichment in ^{15}N through volatilisation in Canterbury than in California. Due to the volume and concentration of the waste in California, significant leakage can also occur. Thus, contamination of groundwater from bulk point sources in the

form of the ponds, and diffuse sources through the spreading of the effluent over land, are present.

In New Zealand, farming practices are different than in California and lead to lower overall and more widespread contamination by nitrate. The only significant stock related point source on a farm is the milking shed where effluent is collected and distributed across the farm in a variety of different methods, depending on what is appropriate for a particular farm (Houlbrooke et al. 2004). While deposition of waste in paddocks is far more widespread and less concentrated than in California. Even the patches of urine discussed in chapter two will not be as significant as compared with the large holding ponds of California. This is a necessary consequences of the lower stocking density and further supports the suggestion that nitrate contaminating groundwater in Canterbury is being sourced from clover. Point sources are less likely to contribute significant amounts of nitrate in the Canterbury setting due to the fact that they do not provide the same volume of waste as in other parts of the world. As a result most nitrate contamination will come from diffuse sources and therefore while nitrate will be elevated across a widespread area it may not reach extreme values as frequently.

In addition to the work in California, other studies also show that stable isotopes can be used to identify nitrate sources. Studies in France (Widory et al. 2004; Widory et al. 2005) were undertaken in a region where the agriculture includes high-level indoor pig farming, poultry and cattle breeding. Practices that result in high stocking rates and significant amounts of concentrated effluent. The land is also extensively fertilised and this is likely to lead to lead to high levels of direct leaching to groundwater. These studies also characterised each end member source by taking samples of the source itself. This is a necessary step in Canterbury if the isotopic composition of nitrate is to be further explored for source determination, as it will provide an expected isotopic signature for each particular source, therefore providing the well-constrained end member compositions that are currently lacking.

A further study in South Korea (Koh et al. 2010) showed that synthetic fertiliser could be identified in paddy fields where it was extensively used and applied in high concentrations, while other nitrate sources in were relatively minor. In residential areas sewerage and wastewater was identified by the higher $\delta^{15}N$ and $\delta^{18}O$ values of nitrate. In both of these areas there was one dominant source of nitrate responsible for the observed elevated concentrations. The simplicity of these systems facilitated stable isotopic forensics. In Canterbury it appears that the number of potential sources, and their diversity in type and contribution, makes identification of the nitrate sources more complex from an isotopic perspective.

4.9. Alternative Contamination Source Tracers

Other studies have also recognised the challenges associated with using nitrate isotopes alone in order to identify nitrate sources to groundwater and surface water. As a result other tracers have been used in conjunction with the stable isotopes in order to improve the accuracy of the identifications. Tracers will vary between sample locations and different sources as their use will be specific particular sources that are involved. Tools used for identification include, boron concentrations and isotopes, chloride/bromide ratios, various micropollutants, and a range of different anions and cations. Some of these indicators may be useful to varying degrees in Canterbury.

4.9.1. Boron

Boron regularly exists in small concentrations in groundwater and contains a wide range of isotopes suggesting that contrasts between different sources may be considerable. Denitrification processes do not affect boron, further making it an appealing co-tracer with nitrate, especially for the identification of mixing. In France (Widory et al. 2004), a combination of boron concentrations and isotopes were able to assist with the identification of wastewater, sewerage and hog runoff. Wastewater and fertiliser were also seen to have

distinct boron isotopic compositions in Nevada, USA (Seiler 2005). The δ11B values for manure range from 19.5 to 42.4‰, from -8 to +7‰ for mineral fertilisers and between 0 and 10‰ for wastewater (Widory et al. 2005). These distinct differences could assist with contaminant source identification in Canterbury, particularly in identifying point sources of either wastewater or manure.

4.9.2. Chloride/Bromide Ratios

Concentrations of both chloride and bromide can be used to identify different sources of contamination to surface and groundwater. Chloride is often used in conjunction with nitrate and has relationships that can further assist with source identification, such as high chloride (1000 mg/L <) and moderate nitrate (2-25 mg/L) concentrations suggesting cattle manure as a source, while moderate chloride (30 mg/L) and high nitrate (60 mg/L <) can be matched to a wastewater source (Widory et al. 2005). Natural groundwater systems that contain a low salinity have often been analysed using the bromide concentration through using it as a ratio with chloride. The ratio also has defined ranges when matched with land use patterns such as ratios from 100 to 300 for areas with no contamination of nitrate and 300 to 800 for areas where residential waste is the main source of nitrate (Koh et al. 2010). Bromide can also be affected through the use of pesticides that may increase the concentration.

4.9.3. Micropollutants

As proposed in chapter two, micropollutants can be used to compliment geochemical data and identify the source to contamination in groundwater. These may take the form of herbicides, pesticides, food additives, and pharmaceuticals. Caffeine has often been used to identify human waste contribution to water as it is often disposed of in high concentrations (Seiler 2005). In Canterbury pharmaceuticals and hormones fed to cattle or other livestock could lead to a better understanding as the contribution to groundwater contamination from the agricultural sources.

Chapter 5 - Conclusions

5.1. Conclusions of the Thesis

The first objective of this thesis was to establish whether nitrate contamination of groundwater and surface water in the Ashburton area could be identified, quantified and traced through the use of stable isotopic analysis. Additional objectives included 1) quantification the effects of nitrate contamination in Ashburton and the wider Canterbury region; 2) exploration of the potential use of coupled isotope-bulk geochemical analysis to track nitrate contamination, and 3) interpretation of the findings in a global context with respect to the scale of the contamination. These objectives sought to inform the tools by which contaminant sources are identified and traced, in addition to the management practices and the effects of anthropogenic derived nitrate sources.

These aims were addressed by specific research questions that sought to explore the distribution of nitrate contamination in groundwater and surface water in Canterbury. This included examining the plume of nitrate that exists down gradient of the AMP plant to establish whether there had been a change in the nitrate concentrations over the past ten years. The research questions also focused on whether the $\delta^{18}O$ $\delta^{15}N$ of nitrate are statistically distinct for different nitrate sources, particularly waste deposited by the meat processing plant. Finally, the extent of the contamination and management practices to reduce contamination was compared with similar locations worldwide.

There are several key findings presented in this thesis. First, nitrate concentrations across the region have increased from 3.65 mg/L in 1983 when regular sampling at the regional council began to 6.98 mg/L in this thesis. Second, nitrate contamination is widespread across the Canterbury Plains, likely indicating a diffuse nitrate source or sources, while extreme levels of contamination (above the MAV), can be linked to more local point sources. While the

increasing contamination trend is concerning, the recognition that an issue exists has led to the implementation of better management practices for disposal of waste containing nitrogen. This is especially the case for point sources of nitrate in the Ashburton area where concentrations have declined over the past ten years.

This finding indicates that the AMP plant, a point source of nitrate, is now contributing less pollution to groundwater than it did in the early 2000's. Immediately down gradient of the plant, nitrate concentrations have decreased by 55% since 1992, presumably due to a change in management practices for waste disposal. In contrast, nitrate concentrations across the region continued to increase. The decreasing AMP nitrate concentrations stand in stark contrast to the pattern of the wider Canterbury region, and represent a water resource management success. In Ashburton the problem was identified and addressed through the implementation of effective management practices via the resource consent process. Nitrate concentrations down gradient of the AMP are now comparable to the rest of the Canterbury Plains aquifer system, a more complicated problem that clearly requires more widespread management measures.

Importantly, the stable isotopic composition of nitrate in groundwater and surface water, in area down gradient of the AMP plant as well as across the Central Canterbury Plains, demonstrate that there is no statistically significant distinction nitrate derived from different sources. This finding is important as it is contrary to other locations around the world such as France (Widory et al. 2004), the United States (Singleton et al. 2005; Panno et al. 2006) and South Korea (Koh et al. 2010). The reasons for this finding are not immediately apparent and several possible mechanisms, including soil processes, the potential presence of a predominant source such as clover that overprints other nitrate source composition, and the farming techniques in the region, are discussed. It is clear that further research is required,

either for the tracing of sources using this tool or exploration of complimentary techniques, such as boron isotopes and tracing of micropollutants.

5.2. A Look to the Future – Management Practices

The greatest challenge faced for managing nitrate contamination is the ability to identify the dominant source of contamination and the specific contribution of each nitrate source. This thesis attempted to use the stable isotopic composition of nitrate with other geochemical factors to identify sources and found that this is not possible for the Canterbury region. Therefore, further research is required to quantify the contribution of each contamination source and subsequently achieve management practices that are targeted and specific, and ultimately more effective.

5.2.1. Point Sources

The specific example of a point source contributor of nitrate to groundwater examined in this thesis was the AMP plant. The results highlight the importance and value of well-planned management practices and monitoring programs. Once it was recognised in the early 1990's that the site was likely to be contributing a significant amount of nitrate to the groundwater, changes made to the way in which waste was disposed of on the site. By implementing measures such as the "cut and carry" technique and reducing the internal cycling of nitrogen on the site, there has been a notable reduction in the nitrate plume (approximately 5% every year since 2000). These practices, combined with the high transmissivity of the aquifer system, demonstrate that it is possible to significantly reduce the effects of a point source of nitrate in the region through best management practices.

The most effective way in which to manage a point source of nitrate, such as the meat processing works, is to control the input of the contaminant to either the surface water or the groundwater. This is a useful management technique for nitrate sources that contribute large

amounts of pollution to groundwater, because if there is a significant enough reduction of inputs made, depending on the local geology, the system has the potential to quickly flush out contaminants and recover. Point sources, however, are much easier to address in this way as they represent a clearly defined source and require only a few individuals or companies to change their behaviours.

5.2.2. Diffuse Sources

Management practices for diffuse sources are more challenging to implement, enforce, and monitor due to the widespread nature of the contamination and the lack of a known dominant source. Sources are generally more difficult to identify and in many cases may be linked with deliberate application of nitrogen (ie fertiliser) to land in order to increase productivity. Thus, economic implications also need to be considered when managing this problem. Furthermore, management of these sources will require the cooperation of a wide range of people, businesses, and organisations that will inevitably lead to an extended period of discussion and acceptable implementation. Erstwhile, all evidence suggests regional nitrate concentrations will continue to rise.

Approaches to managing contamination from diffuse sources, which include fertiliser, dairy runoff, nitrogen fixing feed-crops, and mobilised natural soil nitrate, vary between locations around the world. Management can be put in place either before contamination occurs or be a reactive response through remediation techniques. Multiple management proposals have been made for agriculturally intensive regions of California (Harter & Lund 2012), including, the design of irrigation and drainage systems that reduce percolation, managing plants so that more nitrogen is stored in the biomass, increasing the efficiency of nitrogen fertiliser use and improved storage and handling of fertilisers and manures. The main concern identified with these is the length of time that it will take for the changes to have an effect given the long

travel times of subsurface water. In the Canterbury region, the travel time is varied depending on the depth of the water and local hydrogeology and stratigraphy.

Many of the methods are being explored in Canterbury. Irrigation technologies are improving (Dynes et al. 2010; Moot et al. 2010), not only to more effectively use the water and reduce the volume drawn from wells, but to also reduce the accelerated leaching of contaminants to groundwater. For example, the change from flood irrigation to spray irrigation has assisted in the reduction of the volume of water applied to land (Dynes et al. 2010). Fertiliser use in the region provides a more difficult challenge for future management. There has been a considerable increase in fertiliser use in New Zealand and especially in Canterbury (Statistics New Zealand 2006). In a New Zealand farming environment there is the added complication of complimenting fertiliser with nitrogen fixing feed-crops such as clover (Harris et al. 1995; Woodfield & Caradus 1996; Ledgard et al. 1999). Due to the increase in fertiliser use, there has been a decline in land covered by clover. This increases the amount of nitrogen available to the rest of the biomass as well as the potential for leaching of excess nitrate to underlying water bodies. Excess water from rain, or irrigation, will cause runoff to surface water, accelerated leaching to groundwater or both. As a result, there is the potential for more nitrate contamination to groundwater by using synthetic fertilisers to increase productivity instead of nitrogen fixing plants such as clover as the volume of nitrogen applied through fertilisers is greater than what is biologically fixed by clover (Harris et al. 1995).

Fertiliser use is a source of contamination that has the potential for significant reduction if managed appropriately. Management practices suitable for application in Canterbury include, 1) timing fertiliser application to match the needs of the crop or pasture; 2) ensuring that the application method used is efficient and appropriate; 3) careful application of fertiliser around water recharge areas; and 4) controlling the use of irrigation at the time of fertiliser application (Canter 1997). Of particular importance to Canterbury is the need to complement

the natural nitrogen supplied to plants through biological nitrogen fixation. Research concerning the methods to most effectively farm with clover and added fertiliser is on going (Parfitt et al. 2006; Ledgard et al. 2009) Application of fertiliser near recharge sources is also an important consideration. Careful application will ensure that fertiliser does not directly enter surface water, especially large rivers that recharge down gradient groundwater. Consideration to the timing of application in relation to rainfall and irrigation is also important, as excess water can lead to runoff to surface water or leaching to groundwater (de Klein et al. 2010).

In California, taxation of fertilisers has been proposed (Harter & Lund 2012), as a measure to encourage a reduction in the volume of nitrogen applied to the land and also provide revenue for further protection or remediation measures. In New Zealand, such a measure first requires further research to quantify the significance of the contribution of fertiliser to groundwater contamination. If the contribution were relatively small, such a measure would probably be ineffective and unnecessary.

5.3. A Look to the Future – Nitrate Remediation Techniques

Once nitrate contamination is recognised and the sources are identified, the next important step is to provide a tool for remediation. This may be in the form of treatment or non-treatment of the contaminated water. Non-treatment methods include finding new water sources for drinking, blending clean and contaminated water to dilute contaminants, and land-use management (as outlined above). The first two treatment options can provide drinkable water, however, only land-use management can reduce the excess nitrate that exists in the water systems. Conversely, treatment measures seek to reduce nitrate in the water. Remediation techniques are a reactionary response to contamination issues, however at times they may be the most viable option, such as in California, where little attempt is being made

to reduce nitrate inputs to groundwater. Money and resources are instead being spent on treating contaminated water to ensure it is safe for consumption (Harter & Lund 2012). A treatment measure that could be considered for Canterbury is biological denitrification (Jensen et al. 2012). This involves the conversion of nitrate to nitrogen gas by denitrifying bacteria. Systems exist in many places in Europe and to a lesser extent in the United States, whereby water is abstracted and then treated. Denitrification occurs naturally at low levels. Further denitrification can then be artificially undertaken after water is abstracted.

Non-treatment approaches in Canterbury include abstraction from progressively deeper aquifers. Drinking water in Christchurch is not treated and is typically sourced from deeper wells in order to avoid shallower water that is more likely to be subject to contamination from surface derived pollution sources. This practice is not sustainable for the long term, as contamination will gradually continue to affect water at greater depths. Evidence already exists for this through elevated nitrate concentrations in wells over 200 metres deep (Environment Canterbury 2011). Therefore, either management will need to be in the form of controlling the contamination at the surface, or treating water prior to use.

Drinking water in Canterbury is not treated. However, a continued trend of increasing nitrate contamination of the groundwater may require the exploration of water treatment options. The best treatment option would be to attempt to reduce the volume of nitrate contaminating groundwater and surface water. The simplest of these is care around recharge areas. This is the most effective method for reducing the volume of nitrate contaminating water. In order to achieve this, exclusion zones are required around rivers that may then recharge groundwater aquifers. These zones must be free of animals, deposition of waste and fertilisation. Additionally, planting riparian zones, can remove nitrogen from the soil as plants take it up. If the right conditions are promoted in these riparian zones, denitrification can reduce nitrate

in the subsurface (McKergow et al. 2007; de Klein et al. 2010). Diversion of surface waters and its flow on effects to groundwater systems must also be considered.

5.4. Further Research Prospects

The findings of the thesis create several opportunities for further research on the groundwater contamination issues faced by the Canterbury region. It is important that further research is conducted to better understand current and further threats to the water system, especially as land use intensification continues.

One of the significant findings of this research was the relative homogeneity in nitrate isotopic composition across the region. This led to the conclusion that the dual-isotope approach (ie $\delta^{18}O$ and $\delta^{15}N$) is not a viable approach for source identification on the Canterbury Plains or other New Zealand locations (McLarin et al. 1999). Therefore, further work is required in order to establish what other tracers can be used to quantify the relative contributions of different nitrate sources to the groundwater and surface water bodies. Additional research should be undertaken in order to understand the reason(s) why isotopic compositions are not diagnostic tracers in Canterbury. This could be established through better defining the end member source compositions, which would be achieved by taking samples of manure, fertilisers and other nitrate sources applied to the land. An improved understanding of the processes within the soil could also provide significant information as to the fate of nitrate applied to land and whether these soil processes are masking the isotopic composition of the actual source of nitrate through internal recycling.

Water is a valuable and important resource in the Canterbury region and an understanding of the processes that affect the resource is vital for effective management and the regional economic and environmental well-being and personal health. Sustainable resource management is a challenge that requires critical thinking and adaptation in order to be

successful. Equally important is the willingness of stakeholders to engage in the important process of documenting, identifying and solving resource management problems.

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Appendix 1 – Geochemical Data

Well No.	Northing	Easting	Sample Date	Depth	NO3-N mg/L	HCO3 mg/L	HCO3 mmol/L	1/DIC mg/L	1/DIC mmol/L	δ13C	δD H2O	δ18O H2O	δD Excess	δ15N NO3	δ18O NO3	SD δ15N	SD δ18O
L35/0205	2430392	5742194	15/04/10	28.0							-55.36	-8.49	12.56				
L36/0089	2446257	5737912	15/04/10	68.6							-57.08	-8.55	11.28				
M36/0271	2466511	5737562	16/04/10	25.0							-53.19	-8.38	13.82				
M36/0456	2458795	5729649	16/04/10	9.0							-56.75	-8.81					
M36/0456	2458795	5729649	16/04/10	9.0							-58.19	-8.23	7.63				
M36/8187	2454670	5734013	16/04/10	48.0							-59.11	-8.61	9.77				
M36/8187	2454670	5734013	16/04/10	48.0							-59.11	-8.61	9.77				
L36/0107	2439675	5728287	4/05/10	9.1							-56.27	-8.64	12.87				
L36/2122	2431590	5729290	4/05/10	82.4							-56.22	-8.35	10.57				
L37/0932	2412384	5700180	6/05/10	11.0							-65.23	-9.41	10.09				
L37/0964	2412390	5700124	6/05/10	32.7							-65.35	-9.39	9.80				
M35/1003	2458968	5740156	1/06/10	39.6							-58.71	-8.66	10.56				
M36/4126	2459143	5739207	1/06/10	34.1							-51.16	-7.85	11.65				
L35/0205	2430392	5742194	5/10/10	28.0	6.40	43.16		0.02		-20.58	-51.01	-7.58					
L35/0205	2430392	5742194	5/10/10	28.0	5.23		0.73		1.37	-20.58	-51.01	-7.58	9.64	3.54	3.39	0.21	0.08
L36/0089	2446257	5737912	5/10/10	68.6	9.20	34.53		0.03		-20.01	-54.22	-7.85					
L36/0089	2446257	5737912	5/10/10	68.6	7.68		0.56		1.80	-20.01	-54.22	-7.85	8.58	2.61	1.64	0.16	1.23
L36/0322	2449320	5732085	5/10/10	45.0	12.00	34.53		0.03		-20.76	-50.36	-7.22					
L36/0322	2449320	5732085	5/10/10	45.0	10.12		0.61		1.63	-20.76	-50.36	-7.22	7.37	2.95	2.01	0.09	0.77
L36/0584	2434409	5737609	5/10/10	42.0	12.60	40.70		0.02		-21.52	-58.45	-8.19					
L36/0584	2434409	5737609	5/10/10	42.0	10.65		0.66		1.53	-21.52	-58.45	-8.19	7.04	4.32	2.78	0.28	1.12
L36/1543	2442699	5735434	5/10/10	65.2	12.00	40.70		0.02		-20.65	-50.11	-7.27					
L36/1543	2442699	5735434	5/10/10	65.2	10.12		0.67		1.50	-20.65	-50.11	-7.27	8.02	3.90	1.90	0.18	0.62
L36/2094	2444509	5737700	5/10/10	95.6	6.40	34.53		0.03		-19.24	-52.37	-7.60					
L36/2094	2444509	5737700	5/10/10	95.6	5.23		0.60		1.67	-19.24	-52.37	-7.60	8.42	2.90	2.86	0.26	1.64
M35/1003	2458968	5740156	5/10/10	39.6	13.70	53.03		0.02		-19.97	-53.43	-7.51					
M35/1003	2458968	5740156	5/10/10	39.6	11.61		0.84		1.19	-19.97	-53.43	-7.51	6.67	3.60	2.25	0.10	1.93
M35/5918	2460920	5742845	5/10/10	36.0	4.86	46.86		0.02		-17.10	-55.38	-7.89					
M35/5918	2460920	5742845	5/10/10	36.0	3.88		0.74		1.36	-17.10	-55.38	-7.89	7.76	3.00	2.52	0.17	3.66
M36/0271	2466511	5737562	5/10/10	25.0	6.40	46.86		0.02		-20.33	-52.00	-7.45					
M36/0271	2466511	5737562	5/10/10	25.0	5.23		0.75		1.33	-20.33	-52.00	-7.45	7.59	5.48	2.61	0.12	1.43
M36/0456	2458795	5729649	5/10/10	9.0	8.40	46.86		0.02		-21.38	-55.50	-8.30					
M36/0456	2458795	5729649	5/10/10	9.0	6.98		0.78		1.29	-21.38	-55.50	-8.30	10.90				
M36/2285	2465905	5731377	5/10/10	36.6	7.20	67.83		0.01		-21.14	-57.97	-8.38					
M36/2285	2465905	5731377	5/10/10	36.6	5.93		1.12		0.90	-21.14	-57.97	-8.38	9.08	3.20	1.74	0.07	0.28
M36/4126	2459143	5739207	5/10/10	34.1	10.20	40.70		0.02		-21.08	-52.91	-7.67					
M36/4126	2459143	5739207	5/10/10	34.1	8.55		0.66		1.52	-21.08	-52.91	-7.67	8.42				
M36/8187	2454670	5734013	5/10/10	48.0	8.40	34.53		0.03		-20.41	-59.11	-8.61					
M36/8187	2454670	5734013	5/10/10	48.0	6.98		0.66		1.51	-20.41	-52.78	-7.62	8.14				
L36/0062	2432582	5738811	27/10/10	25.0	7.06	34.53		0.03		-18.13	-55.70	-7.81					
L36/0062	2432582	5738811	27/10/10	25.0	5.81		0.68		1.47	-18.13	-55.70	-7.81	6.80	4.03	1.03	0.16	0.21
L36/0162	2440866	5726412	27/10/10	14.3	12.80	53.03		0.02		-21.77	-52.77	-7.52					
L36/0162	2440866	5726412	27/10/10	14.3	10.82		1.02		0.98	-21.77	-52.77	-7.52	7.36	4.35	2.62	0.40	0.16
L36/0292	2437444	5715595	27/10/10	16.0		28.36		0.04		-12.75	-58.36	-8.37					
L36/0292	2437444	5715595	27/10/10	16.0			0.56		1.78	-12.75	-66.24	-9.70	11.33				
L36/0292	2437444	5715595	27/10/10	16.0			0.56		1.78	-12.75	-58.36	-8.37	8.60	5.94	-8.24	0.09	0.14
L36/0497	2442013	5729119	27/10/10	15.0	3.20	46.86		0.02		-19.25	-55.81	-7.75					
L36/0497	2442013	5729119	27/10/10	15.0	2.43		0.92		1.09	-19.25	-55.81	-7.75	6.17	4.27	0.68	0.04	0.18
L36/1380	2439985	5725462	27/10/10	22.4	12.40	102.36		0.01		-21.23	-54.54	-8.03					
L36/1380	2439985	5725462	27/10/10	22.4	10.47		2.03		0.49	-21.23	-54.54	-8.03	9.66	3.22	0.66	0.11	3.64
L36/1859	2443980	5730460	27/10/10	26.0	2.60	40.70		0.02		-21.99	-56.77	-8.24					
L36/1859	2443980	5730460	27/10/10	26.0	1.91		0.79		1.27	-21.99	-56.77	-8.24	9.18	4.67	0.92	0.05	1.34
L36/2004	2426691	5722181	27/10/10	6.5	1.40	34.53		0.03		-14.43	-58.42	-8.32					
L36/2004	2427030	5722040	27/10/10	6.5	0.86		0.62		1.61	-14.43	-58.42	-8.32	8.11	3.93	-0.55	0.45	1.47
L36/2259	2428659	5733489	27/10/10	25.0	7.60	53.03		0.02		-18.60	-54.08	-7.96					
L36/2304	2434176	5736402	27/10/10	40.0	24.00	34.53		0.03		-20.91	-54.17	-7.82					
L36/2304	2434176	5736402	27/10/10	40.0	20.61		0.69		1.44	-20.91	-54.17	-7.82	8.40	4.97	3.45	0.08	1.71
L36/2359	2442813	5726057	27/10/10	25.0	6.28		0.97		1.03	-18.60	-54.08	-7.96	9.59	5.37	3.20	0.02	0.75
M35/8379	2451628	5748713	27/10/10	6.6		34.53		0.03		-13.40							
M35/8379	2451628	5748713	27/10/10	6.6			0.60		1.67	-13.40	-67.11	-9.86	11.77	1.95	2.51	0.23	1.19
M35/1003	2458968	5740156	1/11/10	39.6	14.06	46.82		0.02			-50.00	-7.64					
M35/1003	2458968	5740156	1/11/10	39.6	11.92		0.68		1.47	-18.23	-50.00	-7.64	11.10				
M36/4126	2459143	5739207	1/11/10	34.1	12.33	34.50		0.03			-50.64	-7.59					

M36/4126	2459143	5739207	1/11/10	34.1	10.41		0.55		1.82	-19.17	-50.64	-7.59	10.05				
L36/0107	2439675	5728287	4/11/10	9.1	5.38	40.70		0.02			-62.27	-8.88					
L36/0107	2439675	5728287	4/11/10	9.1	4.34		0.69		1.45	-21.05	-62.27	-8.88	8.79	4.83	2.04	0.05	0.49
L36/2122	2431590	5729290	4/11/10	82.4	4.00	40.70		0.02			-54.34	-7.93					
L36/2122	2431590	5729290	4/11/10	82.4	3.13		0.66		1.52	-16.40	-54.34	-7.93	9.07	2.69	1.00	0.05	0.50
L37/0403	2411144	5702131	4/11/10	37.8						10.58	307.00	-65.75	-9.54				
L37/0403	2411144	5702131	4/11/10	37.8						-22.61							
L37/0918	2412310	5700390	4/11/10	14.2	11.70					13.11	307.00	-63.28	-9.55				
L37/0918	2412310	5700390	4/11/10	14.2	11.70					-23.37				6.68	1.35	0.01	2.07
L37/0932	2412384	5700180	4/11/10	11.0						-23.46	-57.30	-8.59	11.38				
L37/0932	2412384	5700180	4/11/10	11.0						-23.46							
L37/0964	2412390	5700124	4/11/10	32.7						-22.80	-64.39	-9.21	9.26				
L37/0964	2412390	5700124	4/11/10	32.7						-22.80							
L36/0062	2432582	5738811	30/11/10	25.0	7.20	40.70		0.02									
L36/0062	2432582	5738811	30/11/10	25.0	5.93		0.71		1.41	-18.88	-57.60	-8.78	12.65				
L36/0162	2440866	5726412	30/11/10	14.3	9.80	53.03		0.02									
L36/0162	2440866	5726412	30/11/10	14.3	8.20		0.97		1.04	-23.70	-60.33	-8.93	11.11				
L36/0292	2437444	5715595	30/11/10	16.0													
L36/0292	2437444	5715595	30/11/10	16.0						-11.32	-65.31	-9.76	12.78				
L36/0292	2437444	5715595	30/11/10	16.0						-11.32							
L36/0497	2442013	5729119	30/11/10	15.0	3.00	53.03		0.02									
L36/0497	2442013	5729119	30/11/10	15.0	2.26		1.02		0.98	-22.17	-61.84	-9.17	11.56				
L36/1380	2439985	5725462	30/11/10	22.4	18.20	94.96		0.01									
L36/1380	2439985	5725462	30/11/10	22.4	15.54		1.93		0.52	-22.21							
L36/1859	2443980	5730460	30/11/10	26.0	2.20	40.70		0.02									
L36/1859	2443980	5730460	30/11/10	26.0	1.56		0.76		1.31	-17.45	-63.05	-9.08	9.58				
L36/2004	2426691	5722181	30/11/10	6.5		28.37		0.04									
L36/2004	2427030	5722040	30/11/10	6.5	0.86		0.43		2.33	-14.19	-59.98	-8.71	9.66				
L36/2259	2428659	5733489	30/11/10	25.0	5.35	53.03		0.02									
L36/2304	2434176	5736402	30/11/10	40.0	17.00	45.63		0.02									
L36/2304	2434176	5736402	30/11/10	40.0	14.49		0.77		1.29	-18.81							
L36/2359	2442813	5726057	30/11/10	25.0	4.31		1.05		0.95	-24.34	-60.98	-8.99	10.94				
M35/8379	2451628	5748713	30/11/10	6.6													
M35/8379	2451628	5748713	30/11/10	6.6						-12.46	-57.90	-8.81	12.57				
M35/8379	2451628	5748713	30/11/10	6.6						-12.46							
M35/1003	2458968	5740156	6/12/10	39.6	8.37					-17.81	-56.71	-8.23	9.16				
M36/4126	2459143	5739207	6/12/10	34.1	10.82					-13.43	-58.06	-8.83	12.55				
M35/1003	2458968	5740156	10/01/11	39.6							-56.91	-8.35	9.88				
M36/4126	2459143	5739207	10/01/11	34.1							-57.46	-8.45	10.12				
L35/0205	2430392	5742194	12/01/11	28.0							-61.26	-9.15	11.96				
L36/0089	2446257	5737912	12/01/11	68.6							-57.19	-8.61	11.70				
L36/0584	2434409	5737609	12/01/11	42.0							-59.69	-8.85	11.08				
M35/5918	2460920	5742845	12/01/11	36.0							-60.04	-8.63	9.04				
M36/8187	2454670	5734013	12/01/11	48.0							-62.19	-9.03	10.03				
M36/0271	2466511	5737562	13/01/11	25.0							-55.73	-7.96	7.96				
M36/0456	2458795	5729649	13/01/11	9.0							-59.10	-8.45	8.54				
M36/2285	2465905	5731377	13/01/11	36.6							-57.00	-8.72	12.77				
L36/0062	2432582	5738811	9/03/11	25.0	6.00						-62.50	-9.18	10.97				
L36/0162	2440866	5726412	9/03/11	14.3	9.48						-59.40	-8.70	10.24				
L36/0292	2437444	5715595	9/03/11	16.0													
L36/0497	2442013	5729119	9/03/11	15.0	1.91						-63.19	-8.89	7.95				
L36/0497	2442013	5729119	9/03/11	15.0	1.91												
L36/1380	2439985	5725462	9/03/11	22.4	15.89						-60.29	-8.12	4.63				
L36/1859	2443980	5730460	9/03/11	26.0	1.91						-61.62	-8.66	7.64				
L36/2004	2427030	5722040	9/03/11	6.5							-61.44	-8.71	8.26				
L36/2304	2434176	5736402	9/03/11	40.0	15.76						-60.34	-8.23	5.49				
L36/2359	2442813	5726057	9/03/11	25.0	6.15						-60.97	-8.76	9.14				
M35/8379	2451628	5748713	9/03/11	6.6	0.03												
L35/0826	2432778	5744454	22/03/11	9.6							-65.02	-9.56	11.48				
M36/7716	2455313	5725650	22/03/11	6.5							-60.76	-8.58	7.90				
L36/0292	2437444	5715595	24/03/11	16.0							-62.73	-9.06	9.77				
M35/8379	2451628	5748713	24/03/11	6.6	0.03						-62.07	-9.01	10.01				
L36/0292	2437444	5715595	20/04/11	16.0			0.59		1.68	-12.62	-62.74	-9.16	10.56				
L36/0292	2437444	5715595	20/04/11	16.0			0.59		1.68	-12.62							
M35/8379	2451628	5748713	20/04/11	6.6			0.58		1.71	-13.36	-60.88	-8.87	10.11				

M35/8379	2451628	5748713	20/04/11	6.6			0.58		1.71	-13.36							
M36/7716	2455313	5725650	20/04/11	6.5													
M36/7716	2455313	5725650	20/04/11	6.5										5.21	1.90	0.04	0.03
L36/0062	2432582	5738811	21/04/11	25.0	4.35		0.71		1.42	-18.81	-61.75	-9.05	10.64				
L36/0162	2440866	5726412	21/04/11	14.3	6.33		1.08		0.93	-21.39	-60.33	-8.74	9.58				
L36/0497	2442013	5729119	21/04/11	15.0	1.21		0.99		1.01	-19.97	-62.55	-8.79	7.80				
L36/1380	2439985	5725462	21/04/11	22.4	8.37		1.43		0.70	-20.80	-60.76	-8.27	5.43				
L36/1859	2443980	5730460	21/04/11	26.0	1.44		0.76		1.31	-17.65	-63.12	-8.82	7.46				
L36/2004	2427030	5722040	21/04/11	6.5	0.68		0.60		1.67	-17.07	-62.31	-8.74	7.58				
L36/2304	2434176	5736402	21/04/11	40.0	13.53		0.84		1.20	-19.79	-60.10	-8.46	7.59				
L36/2359	2442813	5726057	21/04/11	25.0	3.41		1.12		0.89	-22.45	-60.90	-8.74	8.99				
L36/0062	2432582	5738811	5/07/11	25.0			0.94		1.06	-18.07	-62.72	-9.39	12.41				
L36/0162	2440866	5726412	5/07/11	14.3			1.25		0.80	-21.75							
L36/0162	2440866	5726412	5/07/11	14.3			1.25		0.80	-21.75							
L36/0292	2437444	5715595	5/07/11	16.0			0.59		1.70		-65.38	-9.50	10.59				
L36/0292	2437444	5715595	5/07/11	16.0			0.59		1.70								
L36/0497	2442013	5729119	5/07/11	15.0			1.00		1.00	-19.20	-63.28	-8.56	5.20				
L36/0497	2442013	5729119	5/07/11	15.0			1.00		1.00	-19.20							
L36/1380	2439985	5725462	5/07/11	22.4			1.59		0.63	-20.82	-61.12	-9.12	11.82				
L36/1859	2443980	5730460	5/07/11	26.0			0.92		1.08	-18.43	-62.38	-8.82	8.19				
L36/2004	2427030	5722040	5/07/11	6.5			0.64		1.56	-16.42	-64.83	-9.39	10.27				
L36/2304	2434176	5736402	5/07/11	40.0			0.94		1.06	-20.61	-60.32	-8.63	8.75				
L36/2359	2442813	5726057	5/07/11	25.0			1.29		0.77	-22.57	-60.70	-8.39	6.41				
L36/2359	2442813	5726057	5/07/11	25.0			1.29		0.77	-22.57							
M35/8379	2451628	5748713	5/07/11	6.6			0.54		1.84	-11.68	-65.94	-9.76	12.12				
L35/0205	2430392	5742194	30/08/11	28.0	5.23									3.54	3.39	0.21	0.08
L36/0062	2432582	5738811	30/08/11	25.0	5.81									4.03	1.03	0.16	0.21
L36/0089	2446257	5737912	30/08/11	68.6	7.68									2.61	1.64	0.16	1.23
L36/0107	2439675	5728287	30/08/11	9.1	4.34									4.83	2.04	0.05	0.49
L36/0162	2440866	5726412	30/08/11	14.3	10.83									4.35	2.62	0.40	0.16
L36/0292	2437444	5715595	30/08/11	16.0										5.94	-8.24	0.09	0.14
L36/0322	2449320	5732085	30/08/11	45.0	10.13									2.95	2.01	0.09	0.77
L36/0497	2442013	5729119	30/08/11	15.0	2.43									4.27	0.68	0.04	0.18
L36/0584	2434409	5737609	30/08/11	42.0	10.65									4.32	2.78	0.28	1.12
L36/1380	2439985	5725462	30/08/11	22.4	10.48									3.22	0.66	0.11	3.64
L36/1543	2442699	5735434	30/08/11	65.2	10.13									3.90	1.90	0.18	0.62
L36/1859	2443980	5730460	30/08/11	26.0	1.91									4.67	0.92	0.05	1.34
L36/2004	2426691	5722181	30/08/11	6.5	0.86									3.93	-0.55	0.45	1.47
L36/2094	2444509	5737700	30/08/11	95.6	5.23									2.90	2.86	0.26	1.64
L36/2122	2431590	5729290	30/08/11	82.4	3.13									2.69	1.00	0.05	0.50
L36/2359	2442813	5726057	30/08/11	25.0	6.28									5.37	3.20	0.02	0.75
L37/0918	2412325	5700393	30/08/11	14.2	11.65									6.68	1.35	0.01	2.07
Ll36/2004	2426691	5722181	30/08/11	6.5	0.86									4.25	-2.04	0.35	3.35
Ll36/2304	2434176	5736402	30/08/11	40.0	20.62									4.97	3.45	0.08	1.71
M35/1003	2458968	5740156	30/08/11	39.6	11.61									3.60	2.25	0.10	1.93
M35/5918	2460920	5742845	30/08/11	36.0	3.88									3.00	2.52	0.17	3.66
M35/8379	2451628	5748713	30/08/11	6.6										1.95	2.51	0.23	1.19
M36/0271	2466511	5737562	30/08/11	25.0	5.23									5.48	2.61	0.12	1.43
M36/2285	2465905	5731377	30/08/11	36.6	5.93									3.20	1.74	0.07	0.28
M36/7716	2455313	5725650	30/08/11	6.5										5.21	1.90	0.04	0.03
L36/2004	2426691	5722181	20/10/11	6.5	0.86									3.93	-0.55	0.45	1.47
M35/8379	2451628	5748713	20/10/11	6.6										1.95	2.51	0.23	1.19
L37/0786-2	2410390	5702990	22/11/11	10.0	3.76	45.80	0.75	0.02	1.33	-20.99				4.36	1.84	0.18	0.83
L37/0158	2417857	5695055	22/11/11	31.2	8.47	64.00	1.05	0.02	0.95	-21.88				3.72	3.49	0.16	1.13
L37/0786	2410390	5702990	22/11/11	30.0	4.79	64.10	1.05	0.02	0.95	-22.42				4.03	1.75	0.15	0.62
L37/0964	2412390	5700124	22/11/11	32.7	7.84	56.80	0.93	0.02	1.08	-22.81				6.47	-0.39	0.15	2.99
L37/1013	2412830	5701770	22/11/11	37.0	5.51	58.00	0.95	0.02	1.05	-22.88				3.44	2.20	0.45	0.92
L37/1195	2414440	5699650	22/11/11	24.0	10.25	58.00	0.95	0.02	1.05	-22.83				3.05	2.21	0.20	0.40
L36/1380	2439985	5725462	25/03/12	22.4	10.48									3.24	3.91	0.07	0.57
L37/0918	2412325	5700393	25/03/12	14.2	11.65									6.53	2.93	0.15	0.46
M35/1003	2458968	5740156	25/03/12	39.6	11.61									2.81	3.25	0.72	0.59
M35/5918	2460920	5742845	25/03/12	36.0	3.88									3.29	4.37	0.28	0.79
M36/0456	2458795	5729649	25/03/12	9.0	6.98									2.93	3.17	0.14	0.69

Appendix 2 – Nitrate Stable Isotope Data

Well No.	Northing	Easting	Depth	Collection Date	NO3-N Conc (mg/L)	δ15N-NO3	δ18O-NO3
L35/0205	2430392	5742194	28	5/10/10	5.228479657	3.535	3.39
L36/0089	2446257	5737912	68.6	5/10/10	7.675741082	2.61	1.64
L36/0322	2449320	5732085	45	5/10/10	10.12300251	2.945	2.005
L36/0584	2434409	5737609	42	5/10/10	10.64741567	4.315	2.78
L36/1543	2442699	5735434	65.17	5/10/10	10.12300251	3.9	1.9
L36/2094	2444509	5737700	95.57	5/10/10	5.228479657	2.895	2.86
M35/1003	2458968	5740156	39.6	5/10/10	11.6088398	3.6	2.245
M35/5918	2460920	5742845	36	5/10/10	3.882485874	3	2.52
M36/0271	2466511	5737562	25	5/10/10	5.228479657	5.475	2.61
M36/2285	2465905	5731377	36.6	5/10/10	5.927697207	3.2	1.735
L36/0062	2432582	5738811	25	27/10/10	5.805334136	4.03	1.025
L36/0162	2440866	5726412	14.3	27/10/10	10.82222006	4.35	2.615
L36/0292	2437444	5715595	16	27/10/10		5.935	-8.24
L36/0497	2442013	5729119	15	27/10/10	2.431609458	4.265	0.675
L36/1380	2439985	5725462	22.4	27/10/10	10.47261128	3.22	0.655
L36/1859	2443980	5730460	26	27/10/10	1.907196296	4.665	0.92
L36/2004	2427030	5722040	6.5	27/10/10	0.858369971	3.9325	-0.54666667
L36/2304	2434176	5736402	40	27/10/10	20.61126575	4.97	3.45
L36/2359	2442813	5726057	25	27/10/10	6.277305982	5.365	3.2
M35/8379	2451628	5748713	6.6	27/10/10		1.95	2.51
L36/0107	2439675	5728287	9.1	4/11/10	4.336977281	4.825	2.035
L36/2122	2431590	5729290	82.44	4/11/10	3.130827008	2.685	0.995
L37/0918	2412310	5700390	14.2	4/11/10		6.675	1.345
M36/7716	2455313	5725650	6.5	20/04/11		5.205	1.9
L35/0205	2430392	5742194	28.0	30/08/11	5.2306796	3.5	3.4
L36/0062	2432582	5738811	25.0	30/08/11	5.807974	4.0	1.0
L36/0089	2446257	5737912	68.6	30/08/11	7.678576	2.6	1.6
L36/0107	2439675	5728287	9.1	30/08/11	4.3381152	4.8	2.0
L36/0162	2440866	5726412	14.3	30/08/11	10.8256712	4.4	2.6
L36/0292	2437444	5715595	16.0	30/08/11		5.9	-8.2
L36/0322	2449320	5732085	45.0	30/08/11	10.1264724	2.9	2.0
L36/0497	2442013	5729119	15.0	30/08/11	2.4324832	4.3	0.7
L36/0584	2434409	5737609	42.0	30/08/11	10.6519224	4.3	2.8
L36/1380	2439985	5725462	22.4	30/08/11	10.4767724	3.2	0.7
L36/1543	2442699	5735434	65.2	30/08/11	10.1264724	3.9	1.9
L36/1859	2443980	5730460	26.0	30/08/11	1.9084344	4.7	0.9
L36/2004	2426691	5722181	6.5	30/08/11	0.8589356	4.3	-2.0
L36/2004	2426691	5722181	6.5	30/08/11	0.8589356	3.93	-0.55
L36/2094	2444509	5737700	95.6	30/08/11	5.2306796	2.9	2.9
L36/2122	2431590	5729290	82.4	30/08/11	3.131682	2.7	1.0
L36/2304	2434176	5736402	40.0	30/08/11	20.618658	5.0	3.5
L36/2359	2442813	5726057	12.0	30/08/11	6.2801784	5.4	3.2
L37/0918	2412325	5700393	14.2	30/08/11	11.6537804	6.7	1.3
M35/1003	2458968	5740156	39.6	30/08/11	11.6131456	3.6	2.2
M35/5918	2460920	5742845	36.0	30/08/11	3.8841264	3.0	2.5
M35/8379	2451628	5748713	6.6	30/08/11		1.95	2.51
M36/0271	2466511	5737562	25.0	30/08/11	5.2306796	5.5	2.6
M36/2285	2465905	5731377	36.6	30/08/11	5.9298784	3.2	1.7
M36/7716	2455313	5725650	6.5	30/08/11		5.2	1.9
L36/2004	2426691	5722181	6.5	20/10/11	0.8589356	3.93	-0.55
M35/8379	2451628	5748713	6.6	20/10/11		1.95	2.51
L37/0964	2412390	5700124	32.7	22/11/11	7.839	6.47	-0.39
L37/1013	2412830	5701770	37	22/11/11	5.506	3.44	2.20
L37/0786	2410390	5702990	30	22/11/11	4.7896	4.03	1.75
L37/0786-2	2410390	5702990	10	22/11/11	3.76	4.36	1.84
L37/1195	2414440	5699650	24	22/11/11	10.24755	3.05	2.21
L37/0158	2417857	5695055	31.2	22/11/11	8.47376	3.72	3.49
L36/1380	2439985	5725462	22.4	25/03/12	10.4767724	3.24	3.91
L37/0918	2412325	5700393	14.2	25/03/12	11.6537804	6.53	2.93
M35/1003	2458968	5740156	39.6	25/03/12	11.6131456	2.81	3.25
M35/5918	2460920	5742845	36.0	25/03/12	3.8841264	3.29	4.37
M36/0456	2458795	5729649	9.0	25/03/12	6.9793772	2.93	3.17

Appendix 3 – Groundwater Field Locations Ashburton

Site Name: L37/0964

ECan Well Number: L37/0964

Grid Ref: 2412390 - 5700124

Location: 9 Grayburn Road, Ashburton

Description: Well on the back of shed. Shed located to the right after entering driveway.

Location Map:

Well Depth: 32.70 m

Diameter: 150 mm

Uses: Domestic

Notes: Owner made an attachment for the wellhead so that the well could have the hose attached to it and be pumped out.

Site Visits:

22/11/2011 Sample: A1221111. Data taken on depth to water, DIC, Temperature, Conductivity, pH, Alkalinity, Samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate and $\delta^{18}O$ and δD of water.

Site Name: L37/1482

ECan Well Number: L37/1482

Grid Ref: 2412830 - 5701770

Location: 99 Taits Road, Ashburton

Description: Down path on left side of house. Beyond swimming pool and next to fence and pump shed.

Location Map:

Well Depth: 36.00 m

Diameter: 150 mm

Uses: Domestic and Garden

Notes: 3 wells present at the location, of varying depths, 10 m (L37/1014), 27 m (L37/1013) and 37 m (L37/1482).

Site Visits:

22/11/2011 Sample: A2221111. Data taken on depth to water, DIC, Temperature, Conductivity, pH, Alkalinity, Samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate and $\delta^{18}O$ and δD of water. Depth to water also taken at other wells.

Site Name: L37/0786

ECan Well Number: L37/0786

Grid Ref: 2410390 - 5702990

Location: 162 Racecourse Road, Ashburton

Description: Up long driveway from the road, house on the left at top of drive. Well located next to pump shed, on left of drive loop, away from the house.

Location Map:

Well Depth: 30.00 m

Diameter: 150 mm

Uses: Domestic and Stockwater

Notes: Sample difficult to access, as pipe that leads into pump shed has to be disconnected to take a fresh sample.

Site Visits:

22/11/2011 Sample: A5221111. Data taken on depth to water, DIC, Temperature, Conductivity, pH, Alkalinity, Samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate and $\delta^{18}O$ and δD of water.

Site Name: L37/0786 - 2

ECan Well Number: Unknown

Grid Ref: 2410390 - 5702990

Location: 162 Racecourse Road, Ashburton

Description: Up long driveway from the road, house on the left at top of drive. Well is located next to pump shed, on left of drive loop, away from the house.

Location Map:

Well Depth: 10.00 m

Diameter: 150 mm

Uses: Domestic

Notes:

Site Visits:

22/11/2011 Sample: A6221111. Data taken on depth to water, DIC, Temperature, Conductivity, pH, Alkalinity, Samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate and $\delta^{18}O$ and δD of water.

Site Name: L37/1195

ECan Well Number: L37/1195

Grid Ref: 2414440 - 5699650

Location: 407 Seafield Road, Ashburton

Description: Well in paddock behind house, next to fence line.

Location Map:

Well Depth: 23.95 m

Diameter: 150 mm

Uses: Domestic and Stockwater

Notes: Owner made an attachment to lift well and access water.

Site Visits:

22/11/2011 Sample: A6221111. Data taken on depth to water, DIC, Temperature, Conductivity, pH, Alkalinity, Samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate and $\delta^{18}O$ and δD of water.

Site Name: L37/0158

ECan Well Number: L37/0158

Grid Ref: 2417857 - 5695055

Location: 101 Buttericks Road, Ashburton

Description: Follow farm track from house. Also accessible from Le Bretons Road.

Location Map:

Well Depth: 31.24 m

Diameter: 300 mm

Uses: Irrigation

Notes:

Site Visits:

22/11/2011 Sample: A6221111. Data taken on depth to water, DIC, Temperature, Conductivity, pH, Alkalinity, Samples for $\delta^{15}N$ and $\delta^{18}O$ of nitrate and $\delta^{18}O$ and δD of water.

Appendix 4 – Flow Velocity Calculation

Flow velocity is calculated as (Thorpe 1992):

$$q = K\frac{H1 - H2}{L}$$

where, K is the Hydraulic conductivity in m^2/ day

H1 and H2 are the pointiometric heads for the start and end of the flow path in m

L is the length of the flow path in m

K values (Bal 1996) for the Ashburton area are between 500 and 630 m^2/day.

H1 was established from well L37/0558, located near AMP and is 37.5 m deep with a water depth of 6.57 m below the measuring point and a measuring point of 96.10 masl.
H2 was established from well L37/0053, located 15 500 m down gradient from AMP and near the coast. It has a depth of 39.3 m and a water depth of 14.7 m from a measuring point 25.58 masl.

L was measured to be 15 500 metres.

Therefore, flow velocity down gradient of AMP is between the following two values.

$$q = 500\frac{89.93-10.58}{15\,500} = 2.46\ \text{m/day}$$

$$q = 630\frac{89.93-10.58}{15\,500} = 3.10\ \text{m/day}$$

Distance from AMP to the coast was measured to be 16 500m. Therefore the time taken for water to travel between AMP and the coast is:

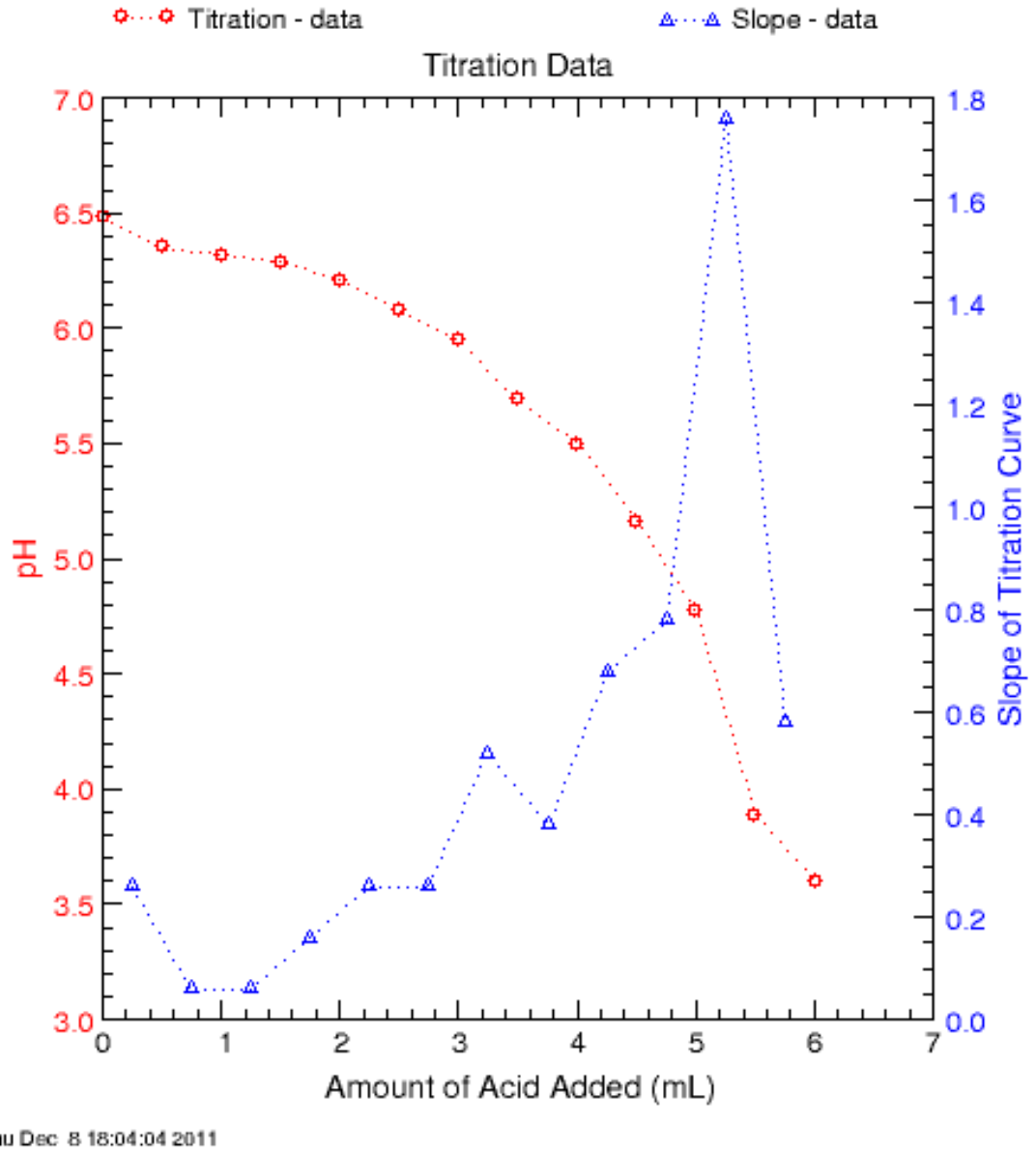
16 500 / 2.46 = 6707 days / 365 = 18.4 years

16 500 / 3.10 = 5322 days / 365 = 14.6 years

Appendix 5 – Ashburton Alkalinity Calculations

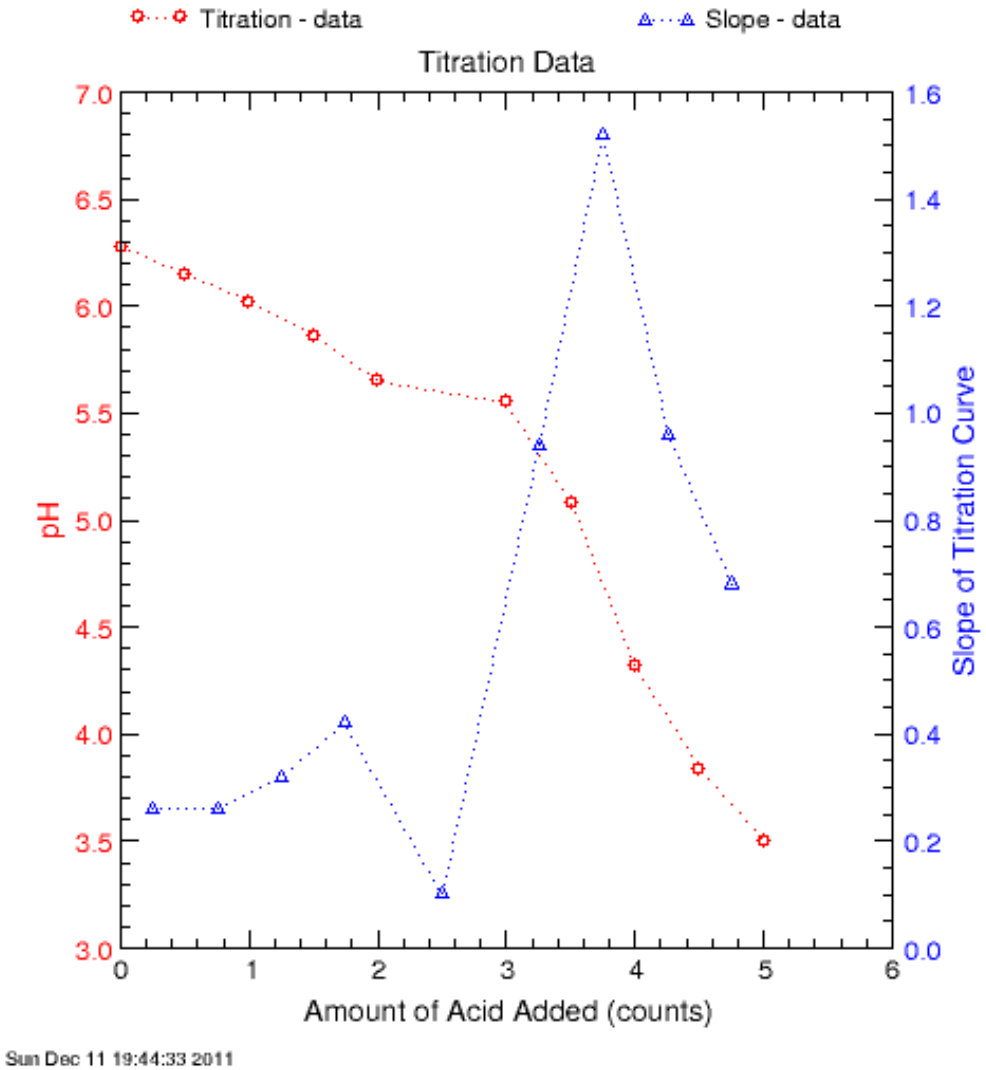
L37/0786

pH	-d(pH)	Counts	d(Counts)	-d(pH)/d(Counts)
6.28		0		
6.15	0.13	0.5	0.5	0.260000
6.02	0.13	1.0	0.5	0.260000
5.86	0.16	1.5	0.5	0.320000
5.65	0.21	2.0	0.5	0.420000
5.55	0.10	3.0	1.0	0.100000
5.08	0.47	3.5	0.5	0.940000
4.32	0.76	4.0	0.5	1.520000
3.84	0.48	4.5	0.5	0.960000
3.50	0.34	5.0	0.5	0.680000



L37/0786-2

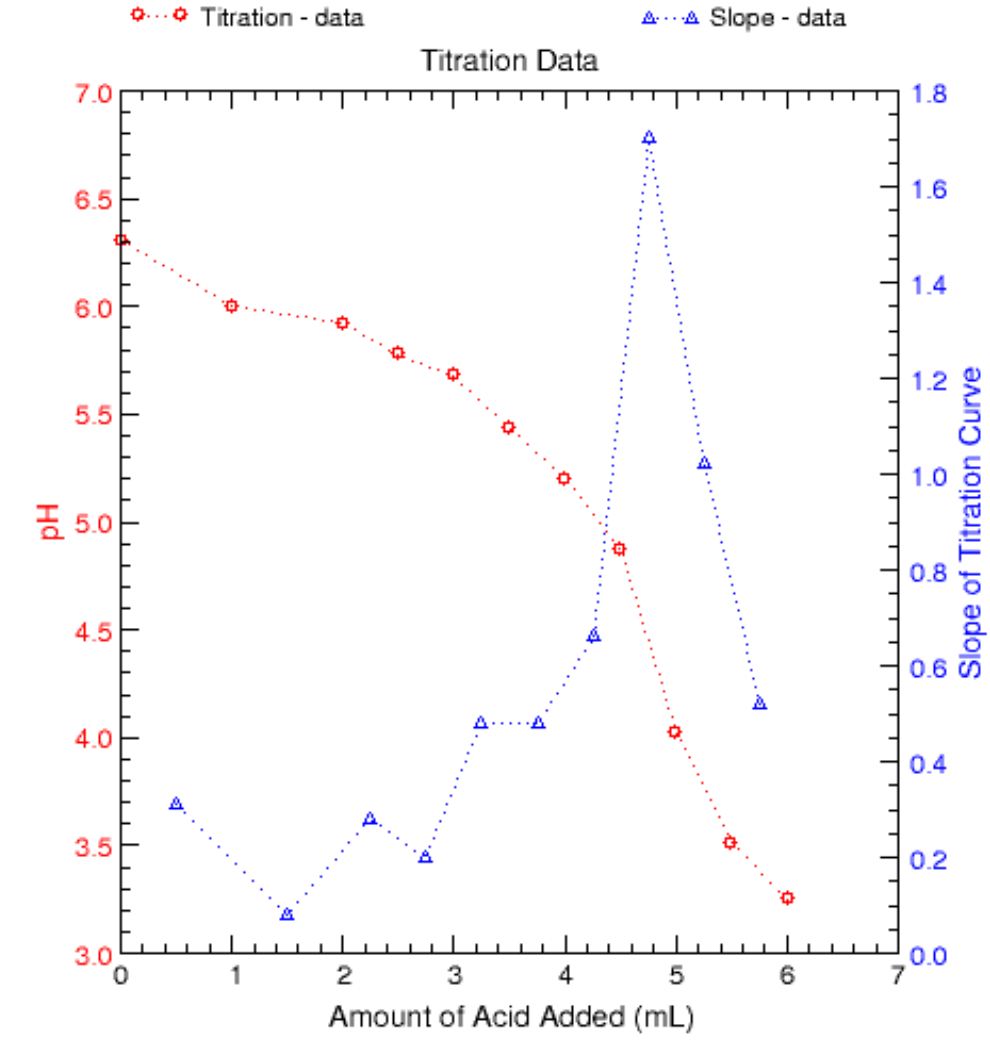
pH	-d(pH)	Counts	d(Counts)	-d(pH)/d(Counts)
6.28		0		
6.15	0.13	0.5	0.5	0.260000
6.02	0.13	1.0	0.5	0.260000
5.86	0.16	1.5	0.5	0.320000
5.65	0.21	2.0	0.5	0.420000
5.55	0.10	3.0	1.0	0.100000
5.08	0.47	3.5	0.5	0.940000
4.32	0.76	4.0	0.5	1.520000
3.84	0.48	4.5	0.5	0.960000
3.50	0.34	5.0	0.5	0.680000



Sun Dec 11 19:44:33 2011

L37/1013

pH	-d(pH)	Volume	d(Volume)	-d(pH)/d(Volume)
6.31		0		
6.00	0.31	1.0	1.00	0.310000
5.92	0.08	2.0	1.00	0.080000
5.78	0.14	2.5	0.50	0.280000
5.68	0.10	3.0	0.50	0.200000
5.44	0.24	3.5	0.50	0.480000
5.20	0.24	4.0	0.50	0.480000
4.87	0.33	4.5	0.50	0.660000
4.02	0.85	5.0	0.50	1.700000
3.51	0.51	5.5	0.50	1.020000
3.25	0.26	6.0	0.50	0.520000



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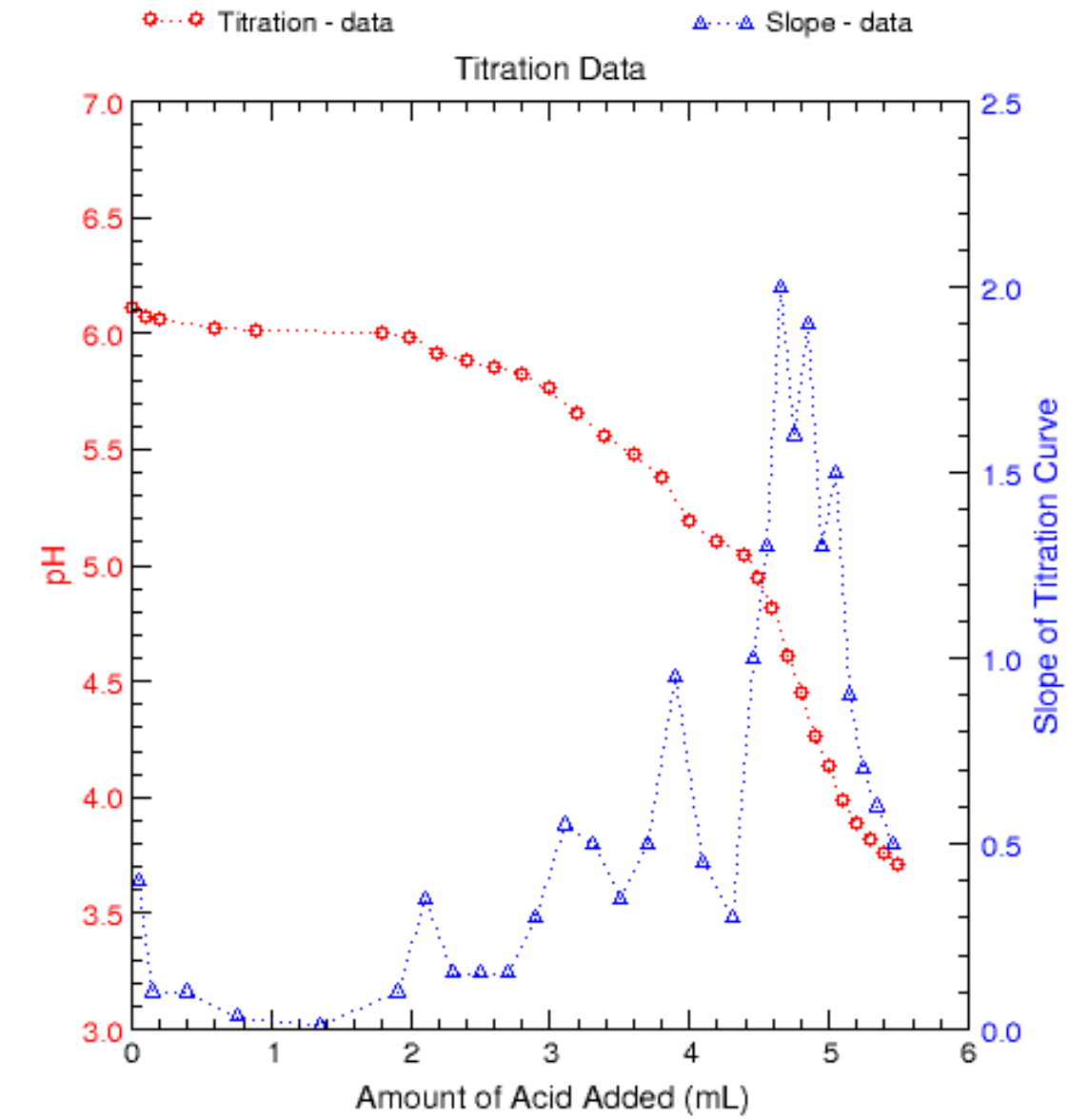
L37/0964

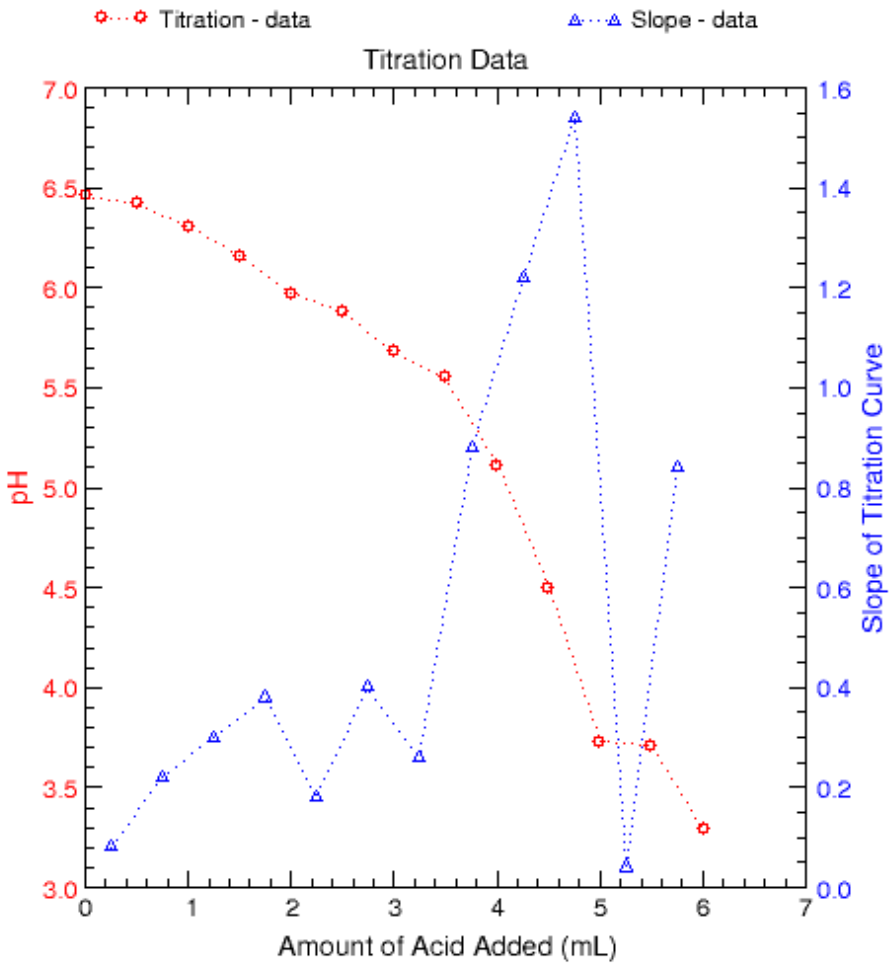
pH	-d(pH)	Volume	d(Volume)	-d(pH)/d(Volume)
6.11		0.0		
6.07	0.04	0.1	0.10	0.400000
6.06	0.01	0.2	0.10	0.100000
6.02	0.04	0.6	0.40	0.100000
6.01	0.01	0.9	0.30	0.033333
6.00	0.01	1.8	0.90	0.011111
5.98	0.02	2.0	0.20	0.100000
5.91	0.07	2.2	0.20	0.350000
5.88	0.03	2.4	0.20	0.150000
5.85	0.03	2.6	0.20	0.150000
5.82	0.03	2.8	0.20	0.150000
5.76	0.06	3.0	0.20	0.300000
5.65	0.11	3.2	0.20	0.550000
5.55	0.10	3.4	0.20	0.500000
5.48	0.07	3.6	0.20	0.350000
5.38	0.10	3.8	0.20	0.500000
5.19	0.19	4.0	0.20	0.950000
5.10	0.09	4.2	0.20	0.450000
5.04	0.06	4.4	0.20	0.300000
4.94	0.10	4.5	0.10	1.000000
4.81	0.13	4.6	0.10	1.300000
4.61	0.20	4.7	0.10	2.000000
4.45	0.16	4.8	0.10	1.600000
4.26	0.19	4.9	0.10	1.900000
4.13	0.13	5.0	0.10	1.300000
3.98	0.15	5.1	0.10	1.500000
3.89	0.09	5.2	0.10	0.900000
3.82	0.07	5.3	0.10	0.700000
3.76	0.06	5.4	0.10	0.600000
3.71	0.05	5.5	0.10	0.500000



Wed Dec 14 20:26:36 2011

L37/1195

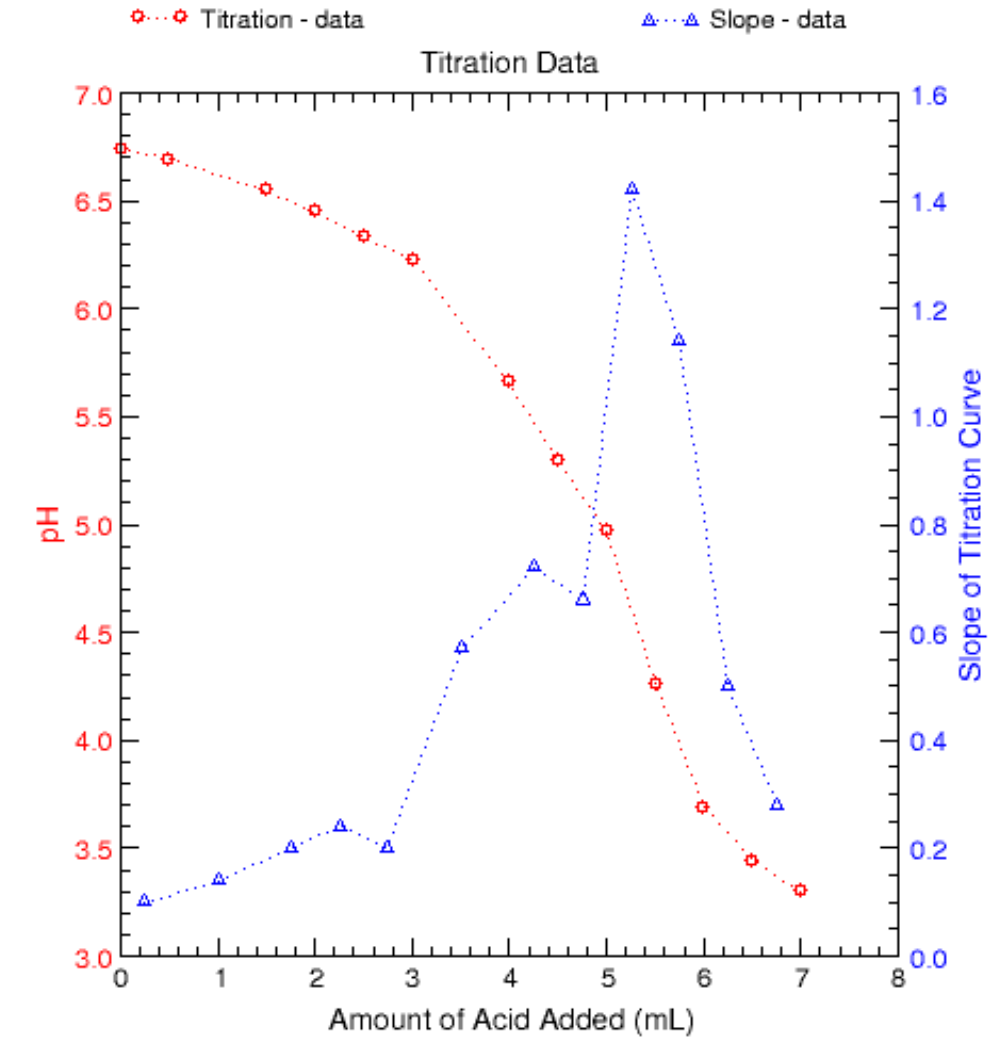
pH	-d(pH)	Volume	d(Volume)	-d(pH)/d(Volume)
6.46		0		
6.42	0.04	0.5	0.50	0.080000
6.31	0.11	1.0	0.50	0.220000
6.16	0.15	1.5	0.50	0.300000
5.97	0.19	2.0	0.50	0.380000
5.88	0.09	2.5	0.50	0.180000
5.68	0.20	3.0	0.50	0.400000
5.55	0.13	3.5	0.50	0.260000
5.11	0.44	4.0	0.50	0.880000
4.50	0.61	4.5	0.50	1.220000
3.73	0.77	5.0	0.50	1.540000
3.71	0.02	5.5	0.50	0.040000
3.29	0.42	6.0	0.50	0.840000



Mon Dec 12 16:55:55 2011

L37/0158

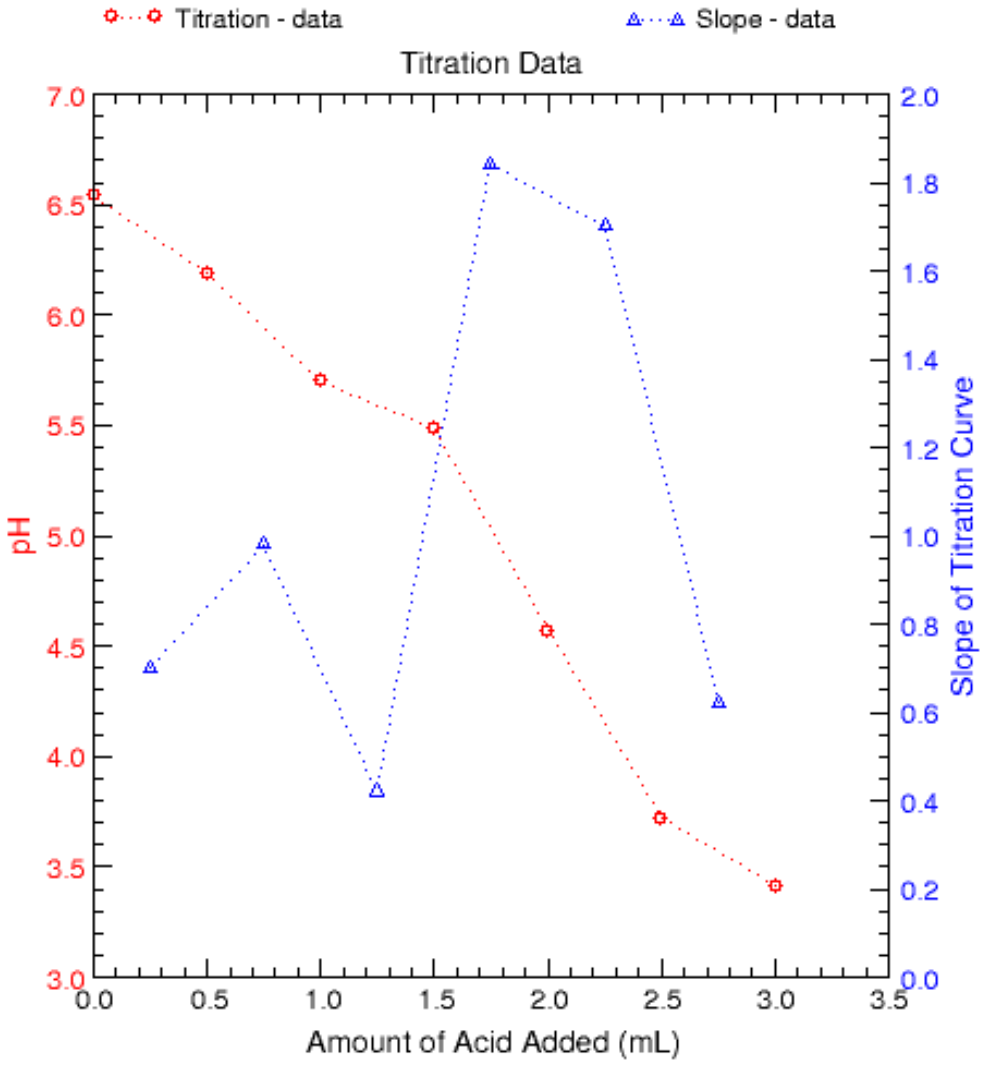
pH	-d(pH)	Volume	d(Volume)	-d(pH)/d(Volume)
6.74		0.0		
6.69	0.05	0.5	0.50	0.100000
6.55	0.14	1.5	1.00	0.140000
6.45	0.10	2.0	0.50	0.200000
6.33	0.12	2.5	0.50	0.240000
6.23	0.10	3.0	0.50	0.200000
5.66	0.57	4.0	1.00	0.570000
5.30	0.36	4.5	0.50	0.720000
4.97	0.33	5.0	0.50	0.660000
4.26	0.71	5.5	0.50	1.420000
3.69	0.57	6.0	0.50	1.140000
3.44	0.25	6.5	0.50	0.500000
3.30	0.14	7.0	0.50	0.280000



Sun Dec 11 19:05:14 2011

Ashburton Domain Stream

pH	-d(pH)	Volume	d(Volume)	-d(pH)/d(Volume)
6.54		0		
6.19	0.35	0.5	0.50	0.700000
5.70	0.49	1.0	0.50	0.980000
5.49	0.21	1.5	0.50	0.420000
4.57	0.92	2.0	0.50	1.840000
3.72	0.85	2.5	0.50	1.700000
3.41	0.31	3.0	0.50	0.620000



Mon Dec 12 17:11:49 2011

Ashburton Business Park Pond

pH	-d(pH)	Volume	d(Volume)	-d(pH)/d(Volume)
6.48		0		
6.35	0.13	0.2	0.20	0.650000
6.00	0.35	0.4	0.20	1.750000
5.87	0.13	0.5	0.10	1.300000
5.73	0.14	0.6	0.10	1.400000
5.55	0.18	0.7	0.10	1.800000
5.24	0.31	0.8	0.10	3.100000
4.75	0.49	0.9	0.10	4.900000
4.28	0.47	1.0	0.10	4.700000
3.99	0.29	1.1	0.10	2.900000
3.81	0.18	1.2	0.10	1.800000
3.68	0.13	1.3	0.10	1.300000
3.60	0.08	1.4	0.10	0.800000
3.53	0.07	1.5	0.10	0.700000